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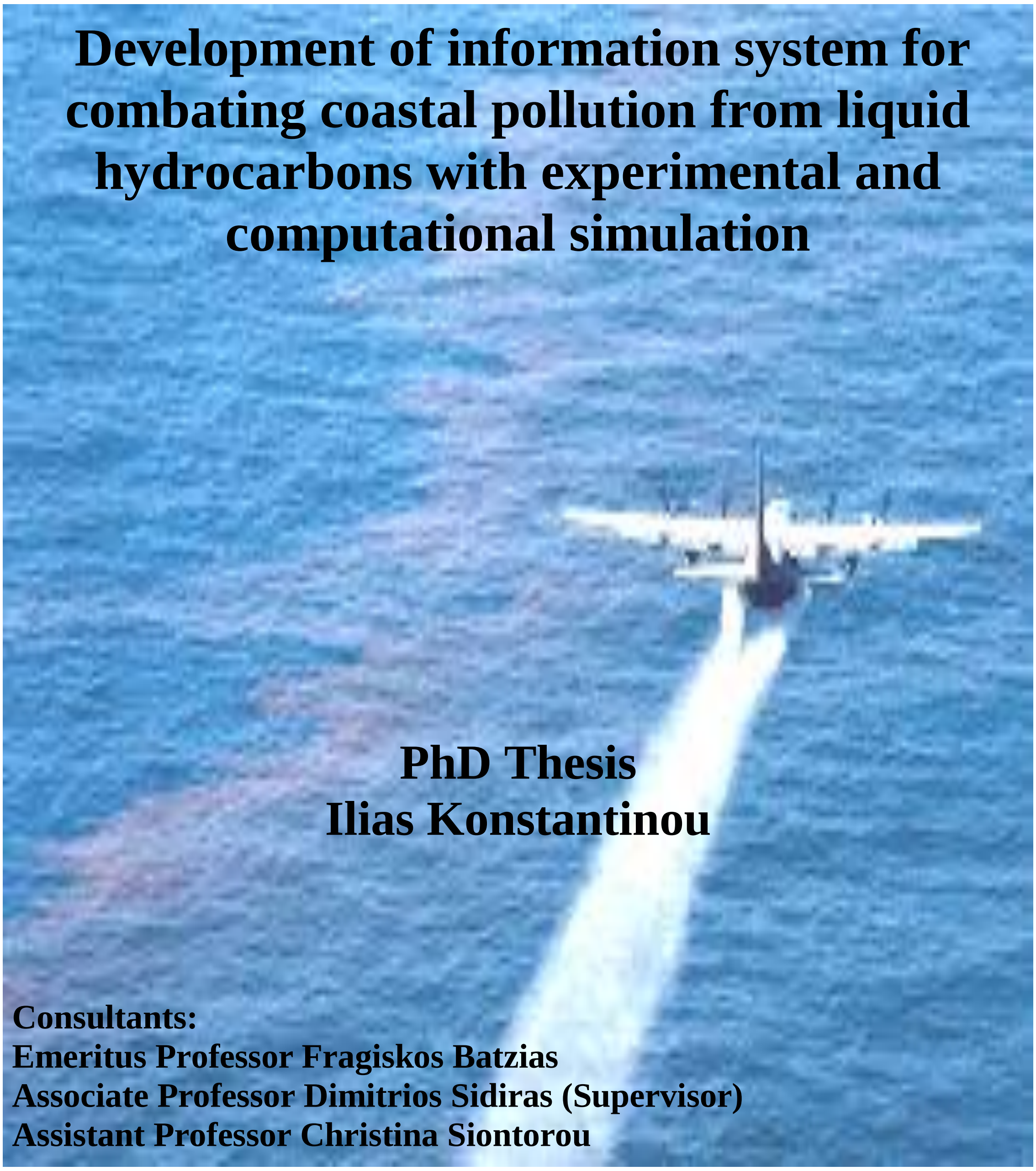

Development of information system for combating coastal pollution from liquid hydrocarbons with experimental and computational simulation

PhD Thesis
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Consultants:
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Associate Professor Dimitrios Sidiras (Supervisor)
Assistant Professor Christina Siontorou

Piraeus, January 2015

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PREFACE

This PhD Thesis is submitted for the degree of Philosophiae Doctor at the Department of Industrial Management and Technology in the School of Maritime and Industry of University of Piraeus. The focus of the Thesis has been to increase the knowledge regarding oil spill management and response. The project and the experiments were carried out from January 2009 to September 2014 as a part-time study during my employment at the Hellenic Coast Guard. The work has been conducted at Laboratory of Simulation of Industrial Processes of University of Piraeus. The Consultants were Emeritus Professor Fragiskos Batzias, Associate Professor Dimitrios Sidiras (Supervisor and Head of the Laboratory) and Assistant Professor Christina Siontorou, all from the University of Piraeus.

The general objective of the PhD project was to develop knowledge, methods and technologies for environmentally beneficial oil spill response strategies mainly in the contingency planning sector and in oil adsorption from novel biomass adsorbents. The PhD project consists of two parts: (I) theoretical; developing a new contingency plan for oil spill response as a part of an information system for combating coastal pollution from liquid hydrocarbons with experimental and computational simulation and (II) experimental; producing a novel oil adsorbent material from lignocellulosic biomass comparable to the commercial oil adsorbents materials.

I wish to express my gratitude to Emeritus Professor Fragiskos Batzias for his eye-opening introductions to new fields and perspectives and for the chance he gave me to develop my knowledge, to my Supervisor Associate Professor Dimitrios Sidiras who helped and offered invaluable assistance, support and guidance and to Assistant Professor Christina Siontorou who continuously supported my work and encouraged me. I would like to acknowledge Professor Michael Tsapatsis, Amundson Chair, Head of the Research Group, Department of Chemical Engineering and Materials Science, University of Minnesota, for FTIR and SEM, Dr. Nick Boukos, Division of Materials Science of the National Center for Scientific Research ‘Demokritos’, for barley straw’s SEM measurements and Dr. Athanasios Batzias for his help about the software system tool of the proposed contingency plan. Financial support provided by the Piraeus University Research Center is kindly acknowledged. During my doctoral studies, the results of the research work have been published, as follows:

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Piraeus, January 2015
The author
Ilias Konstantinou

Dedication

I would like to dedicate this work to my family for the full support during this PhD: to my wife and daughter for their patient and understanding and to my parents, who encouraged me to continue my education and who show me the right way of living.

INTRODUCTION

A short description of the PhD Thesis follows. The Thesis consists of two parts: the theoretical and the experimental. The theoretical part includes chapter from 1 to 6. More specific in chapter 1, an introduction referred to the oil's composition, usage, production and transportation is presented. The causes of oil spills, the chemical processes of spilled oil into the sea and the impacts of oil spills are analyzed in this chapter. Furthermore, the antipollution methods at sea and the clean-up of the oil spilled shoreline as well the disposal of oily waste after recovery are also described.

In chapter 2, the marine environment protection in Greece is presented. The structure of Greek National Contingency Plan; the National and International legislation valid in Greece on the protection of the marine environment; the response mechanism and its weak points are performed. Furthermore the contribution of the involved Services to the response mechanism as well the oil pollution statistics in Greece are also described.

In chapter 3, the Proposed National Contingency Plan is presented. A flowchart that covers an hypothetical event, of either a vessel in danger (with or without an oil leakage) or an oil spill appearance without identifying the source of marine pollution, from the beginning to its efficient handling, is also described. The linguistic variables of combating oil pollution methods (formed by experts in oil spill fields), the methods of combating oil pollution via Rules Index and their combination are also performed.

In chapter 4, a case study of a real oil spill incident, (collision of two ships), is analytically described. Actions that took place are reported and are measured. Theoretical implementation of the Proposed National Contingency Plan for the case study incident is analysed and evaluated. A comparison between the Greek National Contingency Plan, (that was applied in practice), and the Proposed National Contingency Plan is also presented.

In chapter 5, a literature survey about the use of untreated and pretreated lignocellulosic materials as adsorbents for oil spill cleaning is presented. Some of the untreated materials are: barley straw, bagasse, cotton grass fiber, cotton grass mats, rice husk, garlic/onions peels, groundnut husks, peat and walnut shell. Some of the pretreated materials are: acetylated wheat, rice straw and sugarcane bagasse, carbonized fir fibers, pith bagasse and rice husk, fatty acid grafted sawdust, pretreated banana trunk fiber, heated barley straw and NaOH-treated barley straw. Furthermore, in this chapter a literature survey about the use of untreated and pretreated non-lignocellulosic materials as adsorbents for oil spill cleaning is also presented. Some of the above mentioned materials are: organo-clays, exfoliated graphite, expanded perlite, activated carbon, kapok, cocoon, natural wool fibers, recycled wool based nonwoven material, cotton, kenaf bast and moss fiber, kenaf core fiber, cotton treated and raw, sepiolite, waste tire powder and polyurethane foams. Finally, relative adsorption isotherms are described from the literature.

In chapter 6, a multi criteria analysis - choice of adsorbents materials (for oil, dyes, etc.) from modified lignocellulosic biomass and commercial adsorbents is presented. The examined alternatives are: autohydrolyzed wheat straw, sulphuric acid-hydrolyzed wheat straw, sodium hydroxide treated wheat straw, organosolv treated wheat straw and polypropylene oil adsorbent pads. The criteria used are: capital cost, operating cost, health occupational, reliability, environmental friendliness, adsorption efficiency, maturity of technology, contribution to sustainability at local level and marketability within a wider network.

The experimental part includes chapter from 7 to 11. More specific, in chapter 7 the materials used in modification experiments (described in chapter 8) and in adsorbency experiments (described in chapter 9) are presented. Furthermore, the experimental procedure, the laboratory equipments and the analytical techniques of these experiments are also presented. Finally, the procedure of rate batch experiments is described.

In chapter 8, the modification of materials such as wheat straw and barley straw is examined in order to detect if the pretreatment improves the initial adsorption capacities of these materials. Autohydrolysis and acid hydrolysis are selected as modification processes to cover a gap in the literature as they have so far never used again to obtain adsorbents with relatively high sorption capacity, biodegradability and cost-effectiveness for cleaning an oil spill in seawater. The autohydrolysis pretreatment increased the hydrophobicity of straw.

In chapter 9, the materials mentioned in chapter 7 are experimentally measured for their adsorption capacities. The new proposed model for the adsorbency-values measurements is described. Adsorbency tests, (on pure liquids and on oil spills), are performed using, untreated/ pretreated straw, commercial polypropylene oil adsorbent pad “Scorpion P-200” and pom-poms oil trap, as adsorbents. Comparisons of adsorption capacity between untreated/ pretreated straw (wheat and barley) and commercial adsorbents are thoroughly conducted.

In chapter 10, the effect of harvesting year, of net packaging, of chemical dispersant usage and of ageing on wheat straw adsorptivity is studied. According to the ASTM F 726 method, oil adsorbents can be divided in three types: (I) roll, film, sheet, pad, blanket, web (materials which have both linear form and strength sufficient to be handled), (II) loose (materials without sufficient form and strength to be handled) and (III) enclosed, i.e., pillows or adsorbent booms (materials contained by an outer fabric or netting that has permeability to oil but with openings sufficiently small so as to substantially retain the adsorbent material within the fabric or netting). Modified wheat straw belongs to type II, and can be used for cleaning oil spills in shallow water sensitive ecosystems.

In chapter 11, the kinetics of adsorption of oils, (diesel and crude oil) on untreated and pretreated wheat straw, are extensively studied using several kinetic equations and models. Furthermore, kinetic results of oil (diesel oil and crude oil) adsorption are also presented. Finally, in chapter 12, general conclusions and aspects for further research are presented.

CHAPTER 1
OIL AND OIL SPILLS

1.1 Introduction

1.1.1 General

Oil is a general term used to indicate petroleum products which generally consist of hydrocarbons. The word "petroleum" comes from Greek: *πέτρα (petra)* for rocks and Greek: *Ἔλαιον (elaion)* for oil. The term was found in 10th-century Old English sources (Oxford English Dictionary, 2013). Petroleum is classified as a fossil fuel. Origin of petroleum begins with the formation of organic matter, burial of organic matter in a basin maturation of the organic content with pressure temperature at burial depths. Petroleum system includes source rocks, reservoir rocks, reservoir traps, migration paths, seals etc. (Aminzadeh and Dasgupta, 2013). Petroleum is formed by hydrocarbons (a hydrocarbon is a compound made up of carbon and hydrogen) with the addition of certain other substances, primarily sulphur. Petroleum in its natural form when first collected is usually named crude oil can be clear, green or black may be either thin like gasoline or thick like tar and is generally measured in volume (U.S. Environmental Protection Agency, 2011).

1.1.2 Composition of oil

The basic compounds of petroleum are carbon (93% – 97%), hydrogen (10% - 14%), nitrogen (0.1% - 2%), oxygen (0.1% - 1.5%) and sulphur (0.5% - 6%). The specific properties of petroleum source are defined by the percentage of the four main hydrocarbons as part of the petroleum composition. These hydrocarbons are typically present in petroleum at the following percentages: paraffins (15% - 60%), napthenes (30% - 60%), aromatics (3% to 30%), with asphaltics making up the remainder (Golovko et al., 2012). These percentages can vary significantly, giving the crude oil a quite distinct compound personality depending upon geographic region.

Paraffins have a carbon to hydrogen ratio of 1:2, are generally straight or branched chains, but never cyclic compounds. They are used to make fuels. The shorter the paraffins are, the lighter the crude is (El-Hadi and Bezzina, 2005). Napthenes have also a carbon to hydrogen ratio of 1:2, are cyclic compounds and can be thought of as cycloparaffins. They are higher in density than equivalent paraffins and are more viscous (Hayes and Anderson, 1988). Aromatics have a much less hydrogen in comparison to carbon than is found in paraffins. They are more viscous and often solid or semi-solid when equivalent paraffin would be a viscous liquid under the same conditions (Barron et al., 2003). Asphaltics average about 6% in most crude oils; have a carbon to hydrogen ratio of approximately 1:1, making them very dense. They are usually used in road construction (Dickie et al., 1969).

1.1.3 Usage – production – transportation of oil

More than 4,000 years ago, according to Herodotus and Diodorus Siculus, asphalt was used in the building of the walls and towers of Babylon (Chisholm, 1911). The primary use of petroleum was as a lighting fuel.

Fig. 1.1 Seaborne oil trade and number of tanker spills >7 tn, 1970-2011 [ITOPF]

Due to its high energy density and easy transportability, oil has become the world's most important resource of energy since the mid-1950s (U.S. EIA, 2010). The rise in importance was due to the innovation of the internal combustion engine and the rise in mercantile aviation. Petroleum is the key component for many chemical products, as pharmaceuticals, plastics, fertilizers and solvents. 90% of vehicular fuel needs are covered by oil.

Consumption is currently around 84 million barrels per day. Data show that from 1973 to 2009, consumption increased by more than 53.93% (U.S. EIA, 2011). The top three oil producing countries are Saudi Arabia, Russia, and the United States. About 80% of the world's readily accessible reserves are located in the Middle East, with 62.5% coming from the Arab 5: Saudi Arabia, U.A.E., Iraq, Qatar and Kuwait. A large portion of the world's total oil exists in Canada, Venezuela and North Sea. Petroleum's worth as a dense energy source makes it one of the world's most important commodities. Apart from a fall in the early 1980s, seaborne oil trade has grown steadily from 1970 (Fig. 1.1). In 2011, total world oil production amounted to 87 million barrels per day and over one-half was moved by tankers on fixed maritime routes. Chokepoints are narrow channels along widely used worldwide sea routes. They are essential part of international energy security due to the high volume of oil traded through their narrow straits.

Fig. 1.2 The seven main straits trade routes for global oil transportation, [U.S. EIA]

As the international energy market is dependent upon reliable transport the blockage of a main strait (Fig. 1.2), can lead to considerable increases in total energy costs and would affect oil prices adding thousands of miles of transit in an alternative direction.

1.2 Causes of oil spills

1.2.1 General

Petroleum industry involves activities like exploration, production, transportation, processing and refining, storage and product distribution. Each activity is different from another with different general degree of risks involved (Ismail et al., 2012). There are distinct differences even within one type of activity like transportation between land and water transportation or between use of tankers or pipelines. In this subchapter the main causes of oil spills including land-based pollution, and shipping sourced (operationally and accidentally) are demonstrated. An oil spill is the release of a liquid petroleum hydrocarbon into the marine environment, due to human activity, and is a form of pollution. The causes and circumstances of oil spills are varied, but can have a significant effect on the final quantity spilt. For practical reasons, spills are generally categorised by size: <7 tn, small sized oil spills (SSOS), 7-700 tn, medium sized oil spills (MSOS) and >700 tn, large sized oil spills (LSOS), respectively.

1.2.2 Vessel oil pollution

In this study different sized oil spills in terms of the operation that the ship was undertaking at the time of the incident were analyzed. For SSOS and MSOS (Figs 1.3 and 1.4), operations were grouped into Loading/ Discharging, Bunkering, Other Operations and Unknown Operations. Other Operations includes ballasting, de-ballasting, tank cleaning and when the vessel is underway. Reporting of larger spills tends to provide more information and greater accuracy, which has allowed further breakdown of vessel operations. Therefore, operations for LSOS (Fig. 1.5) were grouped into Loading/ Discharging, Bunkering, At Anchor (Inland/ Restricted waters), At Anchor (Open water), Underway (Open water), Underway (Inland/ Restricted waters), Other Operations and Unknown Operations.

During loading and unloading operations of a tanker ship is likely to be caused pollution of the marine environment depending on the bulk, on the loading technique used (silos, pipes, etc.) and on the weather conditions (storm, rain etc.).

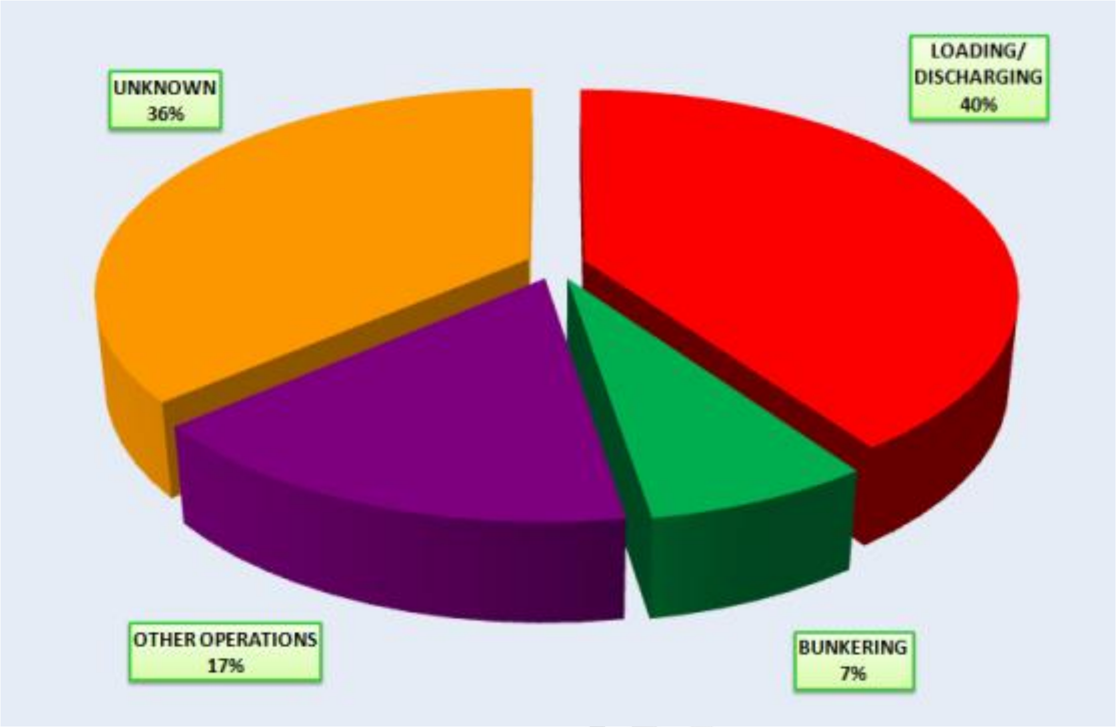


Fig. 1.3 Incidence of SSOS by operation at time of incident, 1974-2012 [ITOPF]

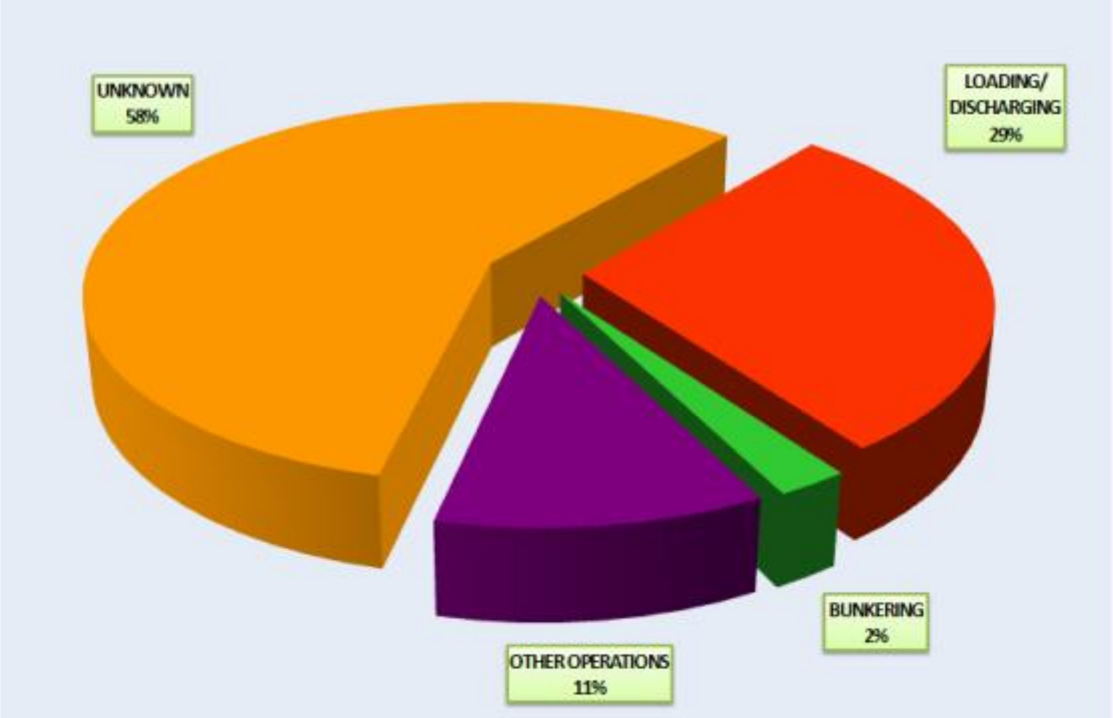


Fig. 1.4 Incidence of MSOS by operation at time of incident, 1970-2012 [ITOPF]

Intentional discharges of substances from the ship is an other subcategory of marine oil pollution and includes oil residues and lubricants produced in the machinery spaces (bilge water) or derived from areas surrounding the load. Since the basis of this wastes is oil, over the years are caused countless micro-spots of oil pollution.

Ballasting and de-ballasting procedures are necessary for tankers' safety as oil tankers are forced by the market structure to execute one of the two trips empty, directed by a petroleum consumer district (e.g. Japan, Western Europe) in a manufacturing and exporting region (e.g., states in the Middle East and North Africa or West) for a new freight receipt. During de-ballasting (i.e. discarded ballast water from cargo tanks at sea), oil cargo residues leaked to the sea and cause significant oil slicks. The usual practice until the 1970's to clean the cargo tanks in order to load new cargo was to wash them with salt water (method Butterworth) with a direct consequence of the discharge of cargo residues into the sea. This method considered as highly oil polluting.

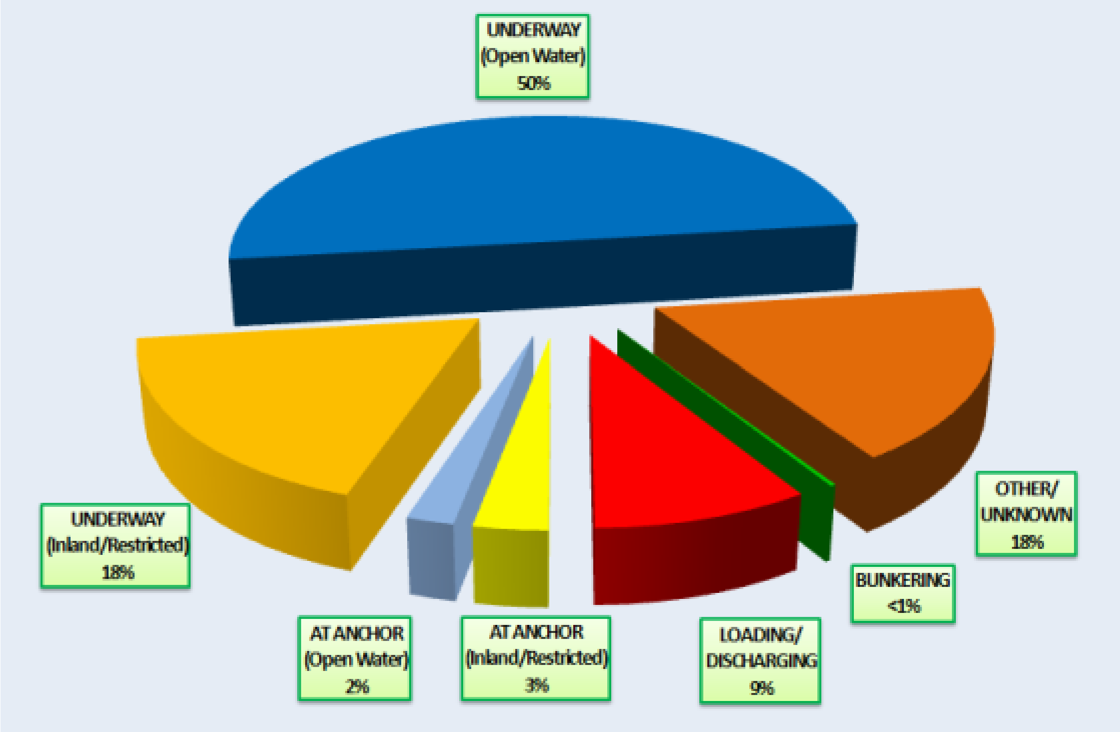


Fig. 1.5 Incidence of LSOS by operation at time of incident, 1970-2012 [ITOPF]

The accidental discharges from tankers divided in two kinds concerns the terminals during loading or unloading and the tanker accidents at sea. Usually, most accidents occurred by tankers near the coast or in areas of heavy traffic. Oil marine pollution caused by accidents of merchant vessels has attracted the immediate interest of the international community since the commercial ships are easy and visible target for immediate review. The reality is quite different because the water pollution (generally, not only oil pollution) from this source does not exceed 12-15% of the total percentage of marine pollution.

In this study different sized oil spills (Figs 1.6, 1.7 and 1.8) in terms of the primary cause of the spill were analyzed. The primary causes have been designated to Allisions/ Collisions, Groundings, Hull Failures, Equipment Failures, Fire and Explosion, and Other/ Unknown. Other causes include events such as heavy weather damage and human error. Spills where the relevant information is not available have been designated as Unknown.

Activities during loading or discharging result in significantly more SSOS or MSOS than LSOS (Figs 1.3, 1.4 and 1.5). SSOS and MSOS account for 95% of all the incidents recorded; a large percentage of these spills, 40% and 29% respectively, occurred during loading and discharging operations which normally take place in ports and oil terminals (Figs 1.3 and 1.4).

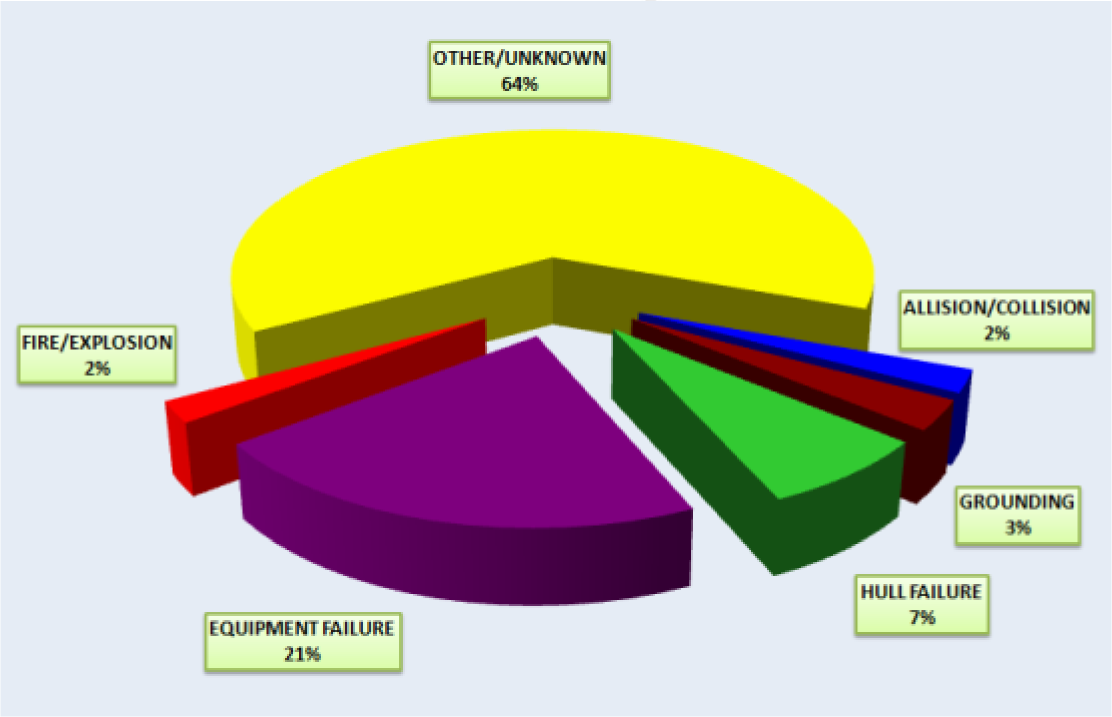


Fig. 1.6 Incidence of SSOS by cause, 1974-2012 [ITOPF]

While the cause of these spills is largely unknown it can be seen that equipment and hull failures account for approximately 28% and 22% of these incidents for SSOS and MSOS, respectively (Figs 1.6 and 1.7). Nevertheless, when considering other operations there is a significant difference in the percentage of allisions, collisions and groundings between these two size groups where we see the percentage increasing from 5% for SSOS to 46% for MSOS (Figs 1.6 and 1.7).

LSOS account for the remaining 5% of all the incidents recorded and the occurrence of these incidents has significantly decreased over the past 43 years. From Fig. 1.5, it can be seen that 50% of LSOS occurred while the vessels were underway in open water; allisions, collisions and groundings accounted for 62% of the causes for these spills (Fig. 1.8). Restricted waters include incidents that occurred in ports and harbours. However, LSOS do still occur (9%) during loading and discharging (Fig. 1.5), and from Fig. 1.8, it can be seen that 16% of these incidents are caused by fires, explosions and equipment failures.

According to one study (Lloyd's, 1990), analyzing 38 cases of marine pollution from tankers, was found that 11 cases resulting in stranding of the ship bottom/ reef (28.9%), 11 cases due to conflicts (28.9%), 8 cases due to fire/ explosion (21%) and 8 cases due to equipment/ hull failure of the ship (21%).

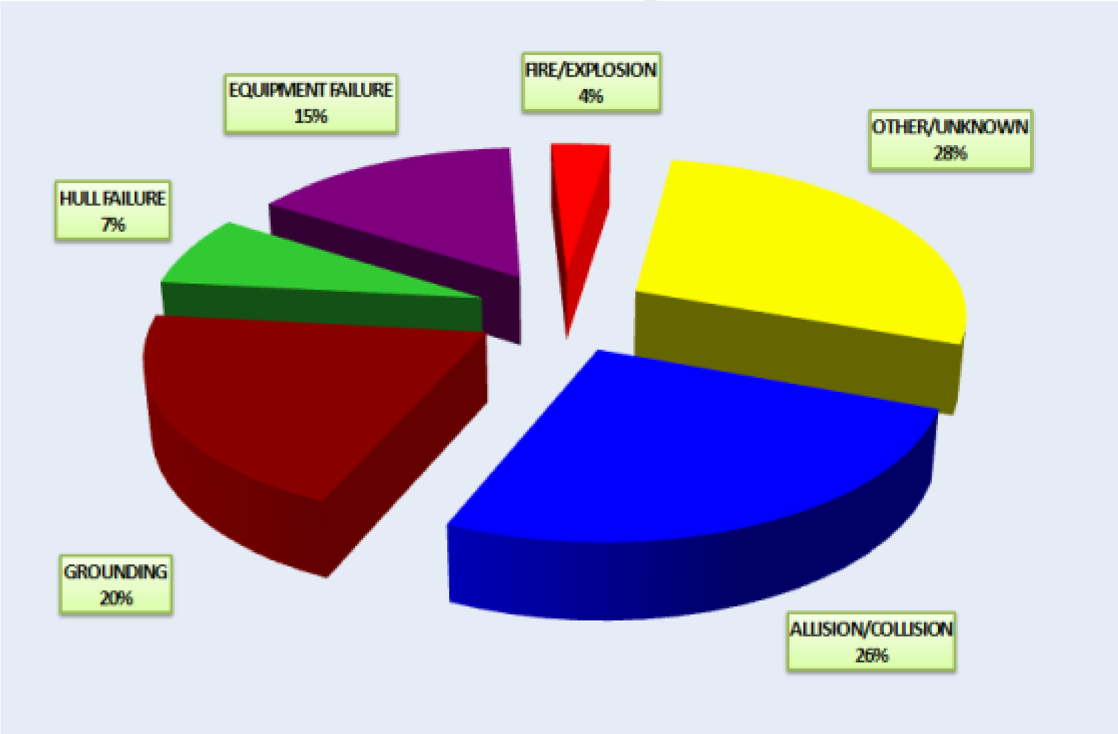


Fig. 1.7 Incidence of MSOS by cause, 1970-2012 [ITOPF]

Moreover, according to another study (ICS & OCIMF, 1990), which analyzes the reasons of the 50 biggest oil spill caused by ships, found that in 14 cases the cause was stranding in bed or reef (28%), in 12 cases the cause was fire/ explosion (24%), in 11 cases was conflict (22%), in 11 cases was equipment/ hull failure of the ship

(22%), and in 2 cases the cause was unknown (4%). The human factors, either individual errors or organizational failures, have been reported to cause as much as 80% of oil spills and marine accidents (DeCola and Fletcher, 2006).

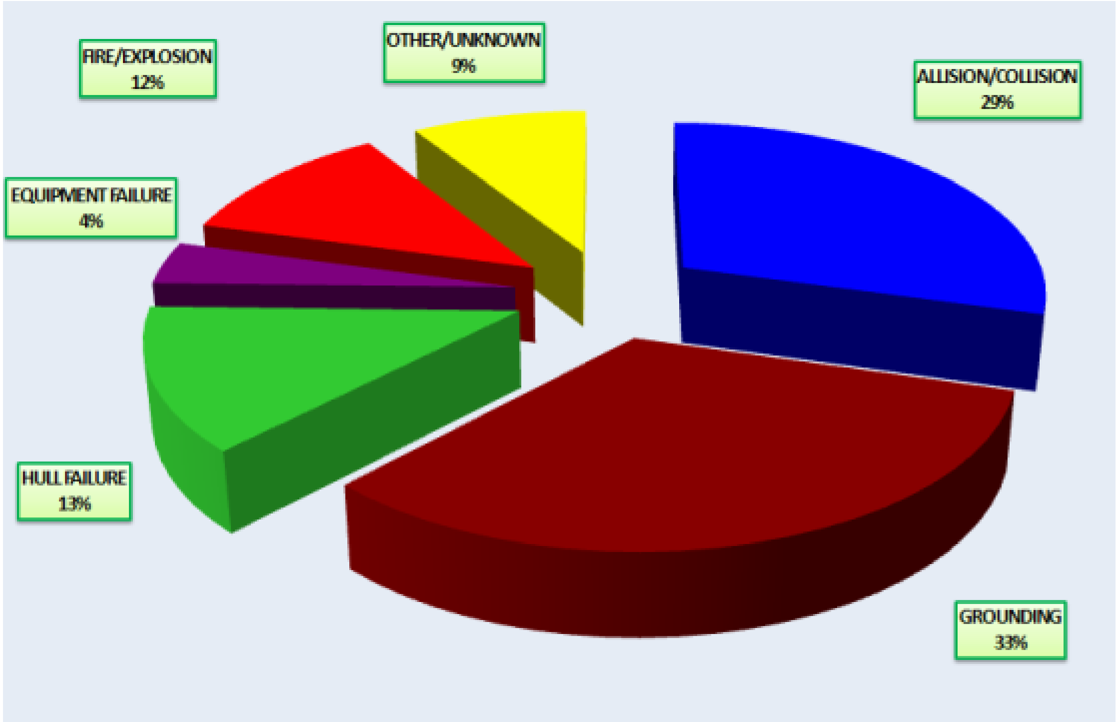


Fig. 1.8 Incidence of LSOS by cause, 1970-2012 [ITOPF]

1.2.3 Other oil pollution

Oil pollution from land-based sources is undoubtedly a significant source of marine pollution. The oil pollutants from the land are usually industrial or land based oil pipelines leakages and oil wastes discharged directly into the sea or through rivers, so marine pollution in coastal areas and semi-enclosed sea areas (bays, gulfs, deltas) is often increased. Oil pollution from mining and exploitation of the continental shelf and the seabed is mainly due to: oil spills from floating rigs or platforms, accidents due to explosions, collisions of such facilities with ships and damage to underwater oil pipelines through contact with passing ships.

The largest percentage of accidental oil input into the sea is associated with oil transportation by tankers and pipelines (about 70%), whereas the contribution of drilling and production activities is minimal, less than 1%, (Patin, 2013).

1.2.4 Number of oil spills worldwide

Large and catastrophic spills belong to the category of relatively rare events and their frequency in recent decades has decreased perceptibly (Patin, 2013). A summary of the 20 major oil spills that have occurred since the Torrey Canyon in 1967 is given in Table 1.1 and the locations are shown in Fig. 1.9.

Table 1.1 Major oil spills 1967-2013, [ITOPF]

Position	Shipname	Year	Location	Spill Size (tn)
1	ATLANTIC EMPRESS	1979	Off Tobago, West Indies	287,000
2	ABT SUMMER	1991	700 n.m. off Angola	260,000
3	CASTILLO DE BELLVER	1983	Off Saldanha Bay, South Africa	252,000
4	AMOCO CADIZ	1978	Off Brittany, France	223,000
5	HAVEN	1991	Genoa, Italy	144,000
6	ODYSSEY	1988	700 n.m. off Nova Scotia, Canada	132,000
7	TORREY CANYON	1967	Scilly Isles, UK	119,000
8	SEA STAR	1972	Gulf of Oman	115,000
9	IRENES SERENADE	1980	Navarino Bay, Greece	100,000
10	URQUIOLA	1976	La Coruna, Spain	100,000
11	HAWAIIAN PATRIOT	1977	300 n.m. off Honolulu	95,000
12	INDEPENDENTA	1979	Bosphorus, Turkey	94,000
13	JAKOB MAERSK	1975	Oporto, Portugal	88,000
14	BRAER	1993	Shetland Islands, UK	85,000
15	AEGEAN SEA	1992	La Coruna, Spain	74,000
16	SEA EMPRESS	1996	Milford Haven, UK	72,000
17	NOVA	1985	Off Kharg Island, Gulf of Iran	70,000
18	KHARK V	1989	120 n.m. off Atlantic coast, Morocco	70,000
19	KATINA P	1992	Off Maputo, Mozambique	66,700
20	PRESTIGE	2002	Off Galicia, Spain	63,000

19 of the largest spills recorded between 1970 and 2002, 95% occurred in the 1970s, 1980s and 1990s, and only 5% occurred in the 2000s. A number of these incidents, despite their large size, caused little or no environmental damage as the oil was spilt some distance offshore and did not impact coastlines.

The incidence of LSOS is relatively low and detailed statistical analysis is rarely possible, consequently emphasis is placed on identifying trends. Thus, it is apparent from Fig. 1.10 that the number of LSOS has decreased significantly during the last 43 years during which records have been kept.

The average number of major spills for the previous decade (2000-2009) is just over three, approximately one eighth of the average for years in the 1970s. A decline can also be observed with MSOS in Fig. 1.11.

Fig. 1.9 Location of major spills [U.S. National Park Service]

1.2.5 Quantities of oil spilt worldwide

The vast majority of spills are SSOS and data on numbers and amounts is incomplete due to the inconsistent reporting of smaller incidents worldwide.

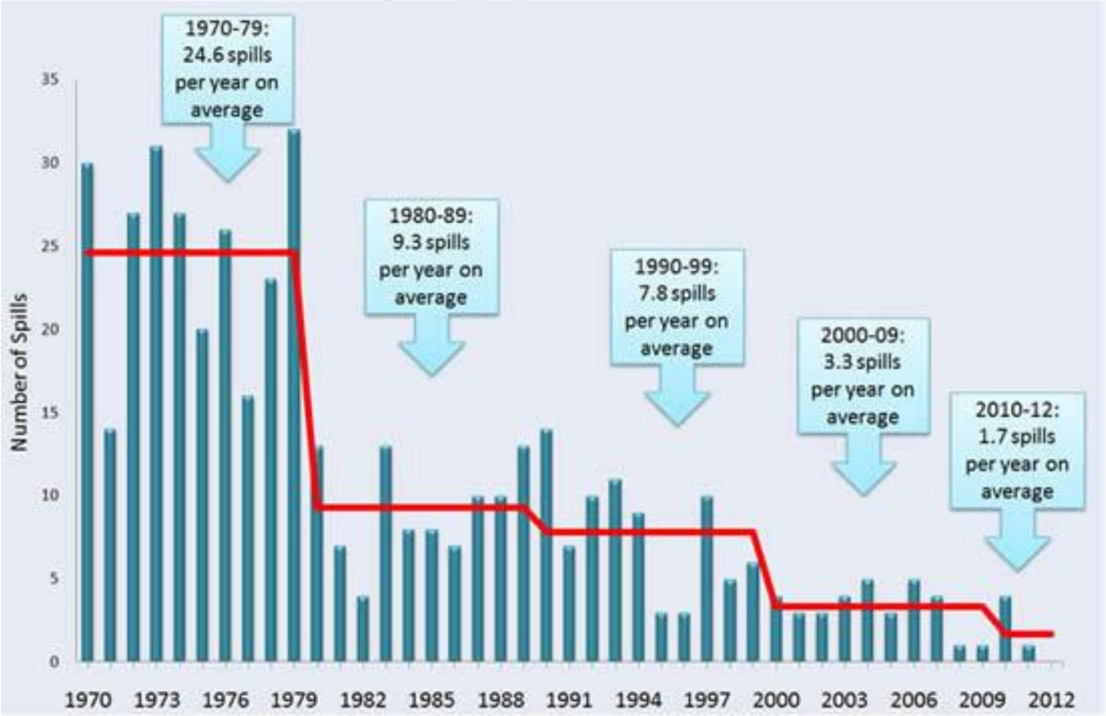


Fig. 1.10 Number of LSOS from 1970 to 2012 [ITOPF]

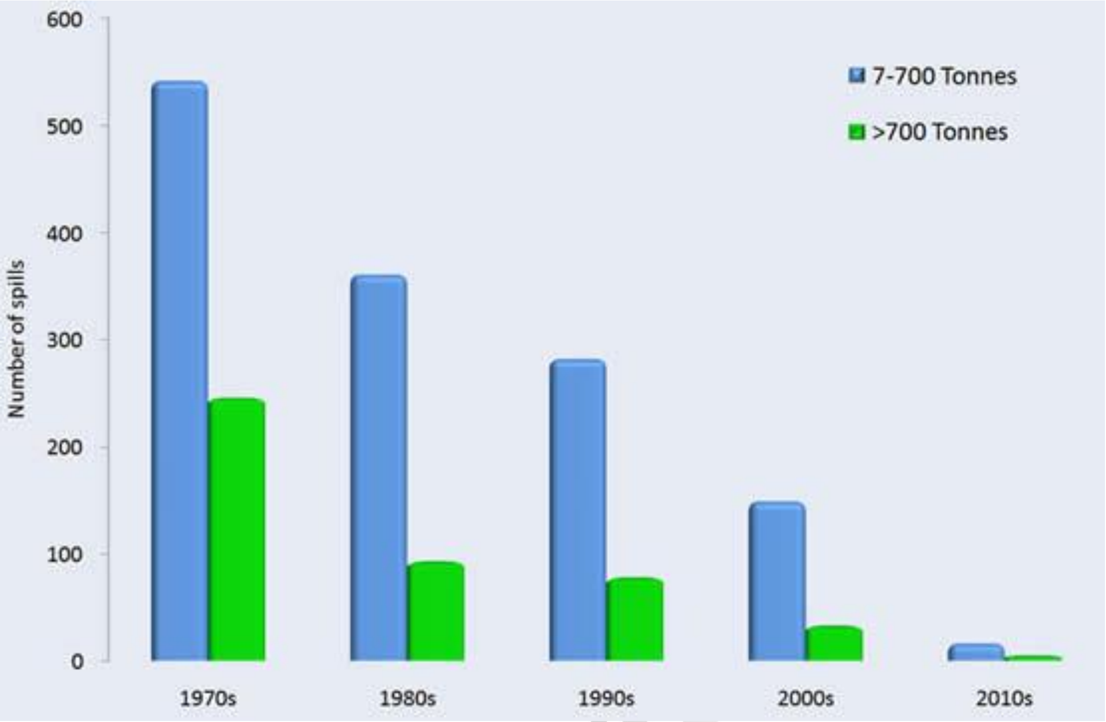


Fig. 1.11 Number of MSOS and LSOS per decade from 1970-2012 [ITOPF]

Reports on spills of LSOS tend to be more reliable. Approximately 5.75 million tonnes of oil were lost as a result of tanker incidents from 1970 to 2012.

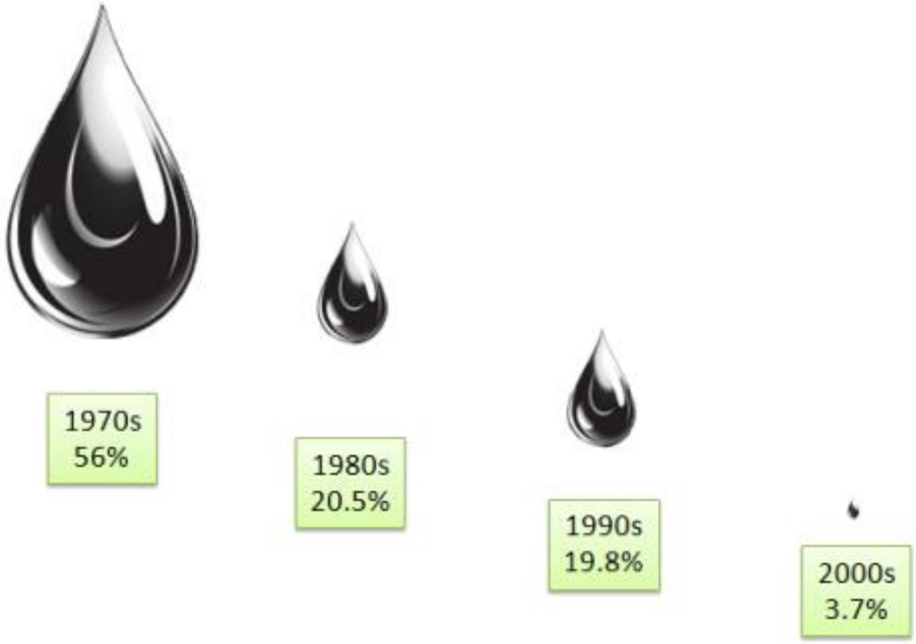


Fig. 1.12 Oil spilt per decade as a percentage of the total spilt, 1970-2009 [ITOPF]

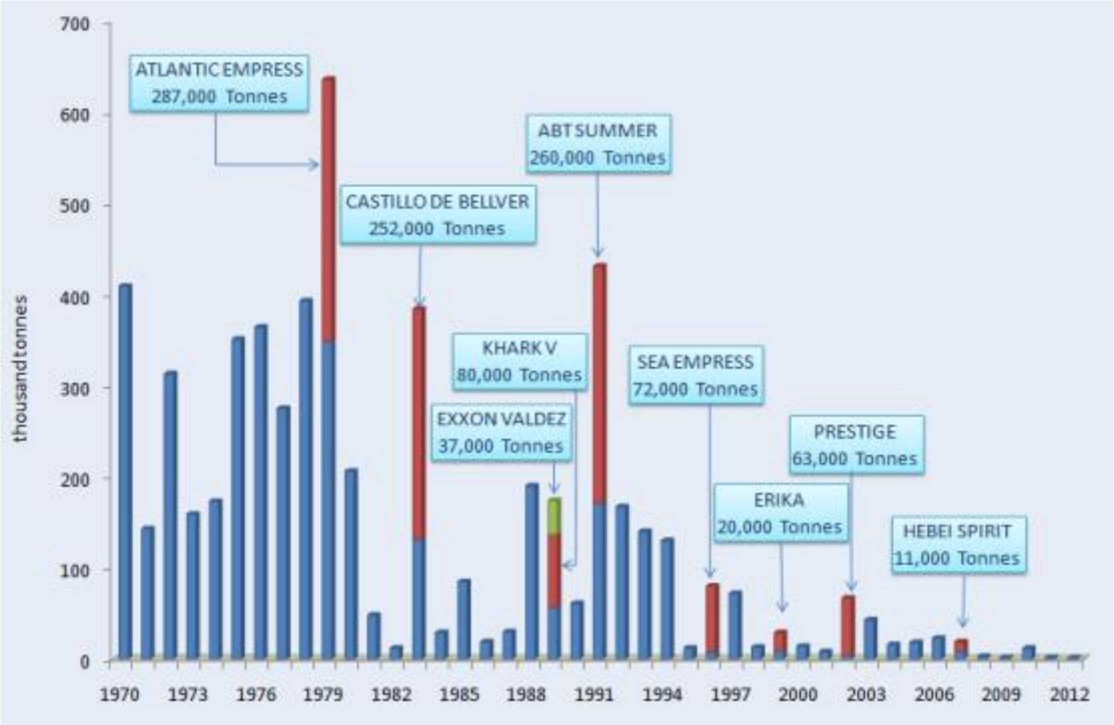


Fig. 1.13 Quantities of oil spilt > 7 tn, 1970-2012 [ITOPF]

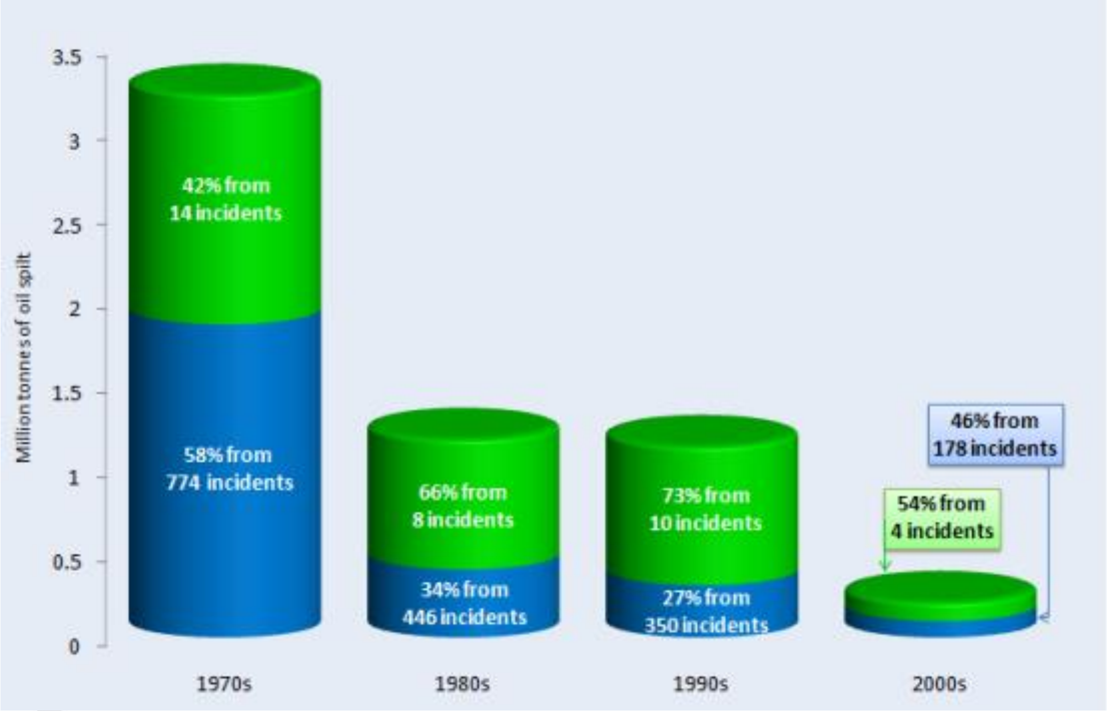


Fig. 1.14 Spills > 7 tn per decade showing the influence of a relatively small number of comparatively large spills on the overall figure [ITOPF]

However, as Figures 1.12 and 1.13 indicate, the volume of oil spilt from tankers demonstrates a significant improvement through the decades. Consistent with the reduction in the number of oil spills from tankers, the volume of oil spilt also shows a marked reduction. As demonstrated in Fig. 1.14, when looking at the frequency and quantities of oil spilt, it should be noted that a few very large spills are responsible for a high percentage of oil spilt.

1.3 Chemical processes of spilled oil into the sea

Oil, when spilled at marine environment, will normally break up and be dissipated into the seawater over time. This dissipation is a result of a number of chemical and physical processes that happen when oil is spilled. The fate of a spill of crude oil or refined product in the marine environment is determined by spreading, evaporation, dissolution, dispersion, emulsification, sedimentation, and various degradation processes.

Most of the weathering processes (evaporation, dispersion, dissolution and sedimentation), lead to the disappearance of oil from the sea surface, whereas others, particularly the emulsification, promote its persistence (Riazi and Edalat, 1996). The quantity and type of oil, the prevailing weather and sea conditions, and whether the oil remains at sea or is washed ashore affect the speed and relative importance of the processes. The main processes that cause oil to weather are described below and summarised in Fig. 1.15.

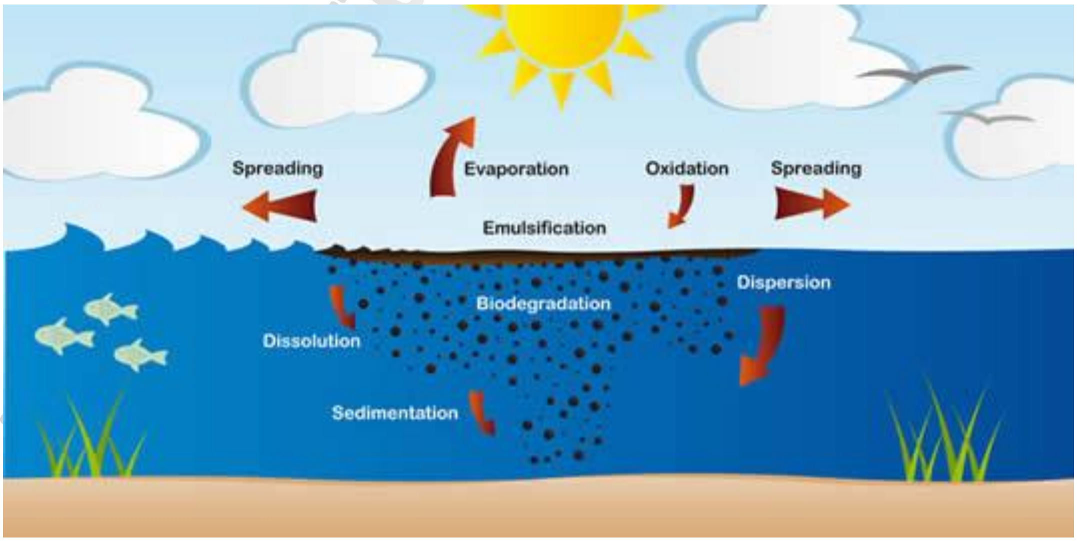


Fig. 1.15 Fate of oil spilled at sea showing the main weathering processes [ITOPF]

Spreading is a complicated process. Oil begins to spread as soon as it is spilled but it does not spread uniformly. Large variations in the thickness of the oil are typical. Any shear in the surface current will cause stretching and even a slight wind will cause a thickening of the slick in the downwind direction (Lehr and Simecek-Beatty, 2000). The speed at which this takes place depends to the viscosity of the oil. Low viscosity oils spread more quickly than those with a high viscosity. This process is driven by gravity and surface-tension forces, and results in increased area being covered by oil (Chebbi, 2000). The slick will begin to break up and will then form thin bands or windrows parallel to the current of air direction, because of winds, wave action and water turbulence. The action of wind, waves, and tidal currents causes drift to occur, which superimposes on spreading motion (Fay, 1971), while the rate at which the oil spreads is also depended to the prevailing conditions.

Evaporation is a vital process for most oil spills. Lighter components of the oil will evaporate to the atmosphere. The oil evaporation is not strictly air-boundary-layer regulated. Time and temperature play an important role in evaporation (Fingas, 2011a). The amount of evaporation and the speed at which it occurs depend upon the volatility of the oil. In a few days, light crude oils can be reduced by up to 75% of their initial volume and medium crudes by up to 40% of their volume (Mackay and Matsugu, 1973). In contrast, heavy or residual oil will only lose about 5% of their volume in the first few days following a spill (Fingas, 1995). Evaporation can increase as the oil spreads, due to the increased surface area of the slick.

Dispersion of oil at sea is a random and very complicated process. Turbulence fluctuations and wave action at the sea surface have recognized random characteristics. The numbers of oil particles and their size are, consequently, also random (Fallah and Stark, 1976). Breaking waves and turbulence cause the oil layer to be propelled into the water column thus forming a “shower” of oil droplets of varying sizes (Korotenko et al., 2000). Some of the smaller droplets will remain suspended in the sea water while the larger ones will tend to rise back to the surface, where they may either coalesce with other droplets to reform a slick or spread out to form a very thin film. This encourages other natural processes such as dissolution, biodegradation and sedimentation to occur. It is likely that the dispersion rate is a function of the slick thickness, oil-water interfacial tension, sea state, and, in particular, the fraction of the sea which is covered by breaking waves (Aravamudan et al., 1982). Natural oil dispersion occurs most quickly if the oil is light and of low viscosity and if the sea is very rough.

Emulsification of oils refers to the process whereby seawater droplets become suspended in the oil. This happens by physical mixing promoted by water turbulence at the sea surface. Emulsification is an important process for certain oils which apparently have chemical constituents which favour the formation and stability of emulsified water. Stable emulsion may contain 80% water, are very viscous, more persistent than the original oil, and have densities approaching that of sea water (Korotenko et al., 2000). These emulsions cause an increase to the volume of pollutant between three and four times. Water-in-oil emulsions are often light brown in colour and referred as “chocolate mousse”. The rate of emulsification increases with increasing sea state (Mackay et al., 1979). Generally, oils with asphaltene content more than 0.5% tend to form stable emulsions which may persist for many months after the initial oil spill, in contrast with oils containing a lower percentage of asphaltenes which are less likely to form emulsions and are more likely to disperse. Finally, emulsions may separate into oil and water again if heated by sunlight under calm sea conditions or when stranded on shorelines.

Dissolution of hydrocarbons from a slick is generally unimportant for the spill mass balance because less than 1% of the oil slick may dissolve into the surrounding water. This depends on the composition and state of the oil, and occurs most quickly when the oil is finely dispersed in the water column. Such a low dissolution of oil is a result of three factors: the low dissolution mass transfer coefficient; the very small water solubility driving force; and the presence of relatively small quantities of the more soluble hydrocarbons, most of which are more susceptible to evaporation (Korotenko et al., 2000). Light aromatic hydrocarbons like benzene and toluene are most soluble in seawater and are also those first to be lost through evaporation, a process which is 10-100 times faster than dissolution (McAuliffe, 1986).

Photo-Oxidation is a process which’s mechanism includes both direct photolysis and also the reaction of reactive oxygen species produced by solar radiation acting on a variety of photo-sensitizers in natural waters. Its extent depends on the type of oil and the form in which it is exposed to sunlight (Lee, 2003). Hydrocarbons react chemically with oxygen either breaking down into soluble products or forming persistent compounds called tars. This process is very slow and even in strong sunlight, thin films of oil break down at no more than 0.1% per day.

When sunlight acts on petroleum the toxicity to the marine life can be increased (Herbes and Whitley, 1983). The oxidation of thick layers of high viscosity oils forms an outer protective coating of heavy compounds (like tar balls that have a solid outer crust surrounding a softer) resulting in the increased persistence of oil.

Sinking and sedimentation processes of oil may happen when as a result of evaporation and emulsification processes its specific gravity is greater than that of the water. However sea water has a density of approximately 1.025 and very few oils are dense enough or weather sufficiently, so that their residues will sink in the marine environment. It is more likely that the presence of sediments will cause a significant portion of the spilled oil to flocculate and then sink to the bottom (Korotenko et al., 2000). Shallow waters are often laden with suspended solids providing favourable conditions for sedimentation. Moreover, oil stranded on sandy shorelines often becomes mixed with sand and other sediments. If this mixture returns back into the sea it may then sink. In addition, if the oil catches fire after it has been spilled, the residues that sometimes form can be sufficiently dense to sink. The size and type of sediments; the salinity and sulphur content of oil; and the degree of agitation affect the adsorption/ desorption of oil onto sediment particles (Kolpack et al., 1977).

Biodegradation is an extremely slow process which only becomes important in the long-term in the removal of oils from the marine environment. Sea water contains a range of micro-organisms or microbes that can partially or completely degrade oil to water soluble compounds and eventually to carbon dioxide and water. Degradation rates are difficult to predict because of high hydrocarbon degradability (such as types and number of microbes), and nutrient and oxygen status of dilution waters (Korotenko et al., 2000). The levels of nutrients (nitrogen and phosphorus) in the seawater, the temperature and the level of oxygen present affect the efficiency of biodegradation. Dispersion increases the area available for biodegradation to take place. Due to the complexity of the process studies of microbe-hydrocarbon interaction usually are carried out under controlled laboratory conditions and then the results are assumed applicable to the marine environments (Feng et al., 1989).

The processes of spreading, evaporation, dispersion, emulsification and dissolution are most important during the early stages of a spill whilst oxidation, sedimentation and biodegradation are more important later on and determine the ultimate fate of the oil.

1.4 Impacts of oil spills

1.4.1 General

Oil spills can cause a wide range of impacts in the marine environment and are often portrayed by the media as ‘environmental disasters’. In a major incident the short-term environmental impact can be severe, causing serious distress to ecosystems and to the people living near the contaminated coastline impairing their quality of life. In time, natural recovery processes are able of repairing damage and returning the system to its normal functions. Long term damage has been recorded in a few instances. However, in most cases, the affected habitats and associated marine life can be expected to have broadly recovered within a few seasons.

1.4.2 Effect on marine environments

The following sections consider the different types of damage caused by ship-source oil spills in various environments. In offshore and coastal waters most oils float on the sea surface and are spread over wide areas by waves, wind and currents. If the release of oil is continuous over time, concentrations of dispersed oil in the upper levels of the water column may be sustained close to the point of release. The accidental oil spills with greatest environmental impact, however, occur in shallow coastal waters where the tidal currents are often large and the water is commonly ‘well mixed’ with no thermo cline or halocline (Thorpe, 2000). Damage in these waters is most often caused by oil becoming mixed into the water column by strong wave action or by the inappropriate use of dispersants too close to the shore.

Shorelines are exposed to the effects of oil more than any other part of the marine environment. However, much of the flora and fauna on the shore are inherently resilient, since they must be able to tolerate the tidal cycle as well as periodic exposure to pounding waves, drying winds, extremes of temperature, variations in salinity through rainfall and other severe stresses. Exposure to the scouring effects of wave action and tidal currents means that rocky and sandy shores are the most resilient to the effects of a spill. This scouring also usually enables natural and rapid self cleaning to take place (Patin, 2013). Oil spills are potentially the most destructive pollution source impacting sandy beaches, affecting all trophic levels. Impacts can be acute and temporary, but they can also be more chronic, lasting for many months or even years (Irvine et al., 2006). Beach morphodynamics and exposure strongly influence the duration of contamination: the coarser the sediment (i.e., reflective beaches), the more rapidly and deeply oil penetrates, sometimes even reaching below the groundwater table (Bernabeu et al., 2006). Persistence and breakdown of stranded oil depends on sand particle size, wave energy, temperature and other factors (Owens et al., 2008).

1.4.3 Effect on plankton, seabirds, marine mammals and reptiles

The pelagic zones of seas and oceans support a myriad of simple planktonic organisms, comprising bacteria, phytoplankton and zooplankton. However, the typically massive over-production of young life stages provides a buffer for recruitment from adjacent areas not affected by the spill, sufficient to make up losses of eggs and larval stages, such that significant declines in adult populations following spills have not been observed. There is not a single known publication in which oil spills have been shown to produce irreversible long-term impact on the planktonic populations of open waters (Patin, 2013).

Seabirds and mammals are among the most vulnerable components of marine ecosystems in relation to oil pollution (Patin, 2013). Sea ducks, auks and other species which raft together in flocks on the sea surface are particularly at risk. Furthermore, oiled plumage reduces the bird’s ability to take off and fly in search of food or to escape predators. There is no clear link between the quantity of oil spilt and the likely impact on seabirds. A small spill during the breeding season, or where large populations of seabirds have congregated, can prove more harmful than a larger spill at a different time of year or in another environment. For many species typically only a small fraction of treated birds survive the cleaning process. Penguins are often an exception and are generally more resilient than many other species. When handled properly, the majority are likely to survive cleaning and rejoin breeding populations.

Whales, dolphins and other cetaceans may be at risk from floating oil when surfacing to breathe or breach. However seals and other marine mammals that haul-out or spend time onshore are more likely to encounter and suffer from the effects of oil. Floating oil may be a threat to marine reptiles, such as turtles, marine iguanas and sea snakes. Rehabilitated sea turtles, when compared with other reptiles, had the highest chances of survival after being exposed to an oil spill (Mignucci-Giannoni, 1998).

1.4.4 Effect on sea grass, corals and mangroves

The impact of oil on sea grasses varies depending on the type of oil spilt, the degree of contact and the species of sea grass (Taylor and Rasheed, 2011). Floating oil is most likely to pass over sea grass beds with no damaging effects. However, if oil or its toxic components become mixed into shallow inshore waters at sufficiently high concentrations, sea grass and associated organisms may be impacted. Corals are highly sensitive organisms that can take a long time to recover from oiling. Dispersed oil presents the greatest risk of damage to coral reefs. Laboratory experiments indicated that corals do not exhibit mortality associated with oil spills unless the oil is dispersed into subsurface seawater (Knap, 1987). Mangroves are salt-tolerant trees and shrubs growing at the margins of sheltered tropical and sub-tropical waters. They are highly vulnerable to oil spills. Studies of the effects of oil spills on mangroves have reported a variety of responses ranging from no observed effect to widespread seedling mortality and dieback of mature trees (Grant et al., 1993).

1.4.5 Effect on tourism

Tourism industries are one of the most economically important set of industries worldwide, yet they are also one of the most susceptible and vulnerable to crises or disasters (Pforr, 2009). Tourism is a basic economic sector in coastal areas that can be disrupted by the presence of oil in the seawater or on the shoreline, with the most severe consequences likely to arise just before or during the key tourist season. Interruption of coastal activities such as bathing, boating and diving can have a consequent effect for hotels, camp sites and the many other businesses and persons who live from tourism.

Holidaymakers may decide to cancel bookings in the area affected and transfer their holidays to alternative locations. Many industries (e.g., accommodation, transport) and sub industries (e.g., hotels, airlines, rental cars, and rail or sea transport companies) interact with each other so the economic damage increases (Ritchie et al., 2013). Oil affected beaches may have to be closed during clean-up. On beaches that remain open, in addition to the remaining oil, the presence of workers and equipment may cause a nuisance.

The U.S. Travel Association estimates that the economic impact of the oil spill on tourism across the Gulf Coast over a three-year period could exceed approximately 23 billion $, in a region that supports more than 400,000 travel industry jobs generating 34 billion $ in revenue annually (Oxford Economics, 2010). From the other hand, the possibility of the presence of a wreck close to the shoreline can attract substantial numbers of spectators bringing with them the possibility that some businesses, (cafés, restaurants, etc.), may be able to make up some of their losses. In the long term, such destinations, industries, or sub industries may capture the benefits of this displaced demand, heightened media attention, and may even develop new product in some cases (Williams and Ferguson, 2005).

1.4.6 Effect on aquariums, recreational facilities, marinas, and ports

The operation of many coastal facilities, such as aquariums, swimming pools and thalassotherapy centres, require a continuous supply of fresh seawater. Although the water is usually screened to eliminate debris and sometimes passed through filter beds, soluble components of the oil may still get into the water supply causing serious problems to the function of the above mentioned facilities.

Marinas are usually enclosed by sea defences to protect moored vessels against adverse sea conditions. The sea defences are often provided by rock armour or tetra pods and if these oiled, can be difficult to clean. Ports can suffer similar problems, although on a considerably larger scale, and many port authorities demand that the hulls of commercial vessels are cleaned before the ships are permitted to sail. Considerable disruption may be caused to normal port operations while vessels undergo cleaning or if vessel movements have to be curtailed. Statistical records show that shipping casualties frequently occur close to the coast and in the approaches to ports. Disruption to port operations and potentially to businesses served by the port may necessitate alternative routes for the movement of goods and materials.

1.4.7 Effect on industrial water intakes and desalination plants

Seawater is widely used in a broad range of industries: as a coolant for thermal and nuclear power stations, refineries etc. In electricity utilities and process plants located in coastal zones, seawater is frequently used directly in heat exchangers and condensers (Pugh et al., 2005). Electricity power plants use cold seawater circulated through tubes to condense steam from steam turbines. The possibility that oil will be entrained into the water flow depends on the type of oil, the weather conditions at the time of the spill and the design of the intake itself.

As regards the effect on desalination plants, oil is a threat for two reasons; it contains pollutants not normally found in seawater that desalination facilities do not normally have to remove and the most obvious reason is the damage it can do to sea water intake filter and heat exchangers (Al Malek and Mohamed, 2005).

Oil in seawater can take the form of the well recognized slick, but it can also form large tar balls and sunken oil globs that can be drawn into intake filters. Obviously, the oil can then foul the filter, hence limiting the amount of water intake, as well as foul internal membrane and disrupting the reverse osmosis process (Lovell, 1998).

1.4.8 Effect on health, heritage sites-artefacts, fisheries and salt production

The unpleasant smell of oil stranded or floating close to the shoreline presents a severe nuisance to population living along the affected coastline. A major oil spill is likely to raise health concerns and complaints of breathing difficulties and headaches. Cultural artefacts may be damaged, either through direct contact with oil or as a result of clean-up operations. The cleaning of heritage sites requires equivalent care and sensitivity as the surfaces of ancient buildings which have oil weathered become porous.

An oil spill can directly damage the boats and gear used for catching or cultivating marine species. A common cause of economic loss to fishermen is interruption to their activities by the presence of oil or the performance of clean-up operations. An adverse impact of oil spills on fish is most likely to be observed in the shallow coastal areas of the sea where the water dynamics are slow. Fish in early life stages are known to be more vulnerable to oil, compared to adults, and, therefore, some younger fish may be killed by exposure to high concentrations of toxic components of crude oil (Patin, 2013).

In regions with limited rainfall, salt is often produced by the evaporation of seawater in salt pans along the shoreline. If an oil spill occurs, oil can be prevented from entering the ponds by closing the sluice gates. However, if pollution is prolonged, it may be possible to maintain production by allowing seawater into the ponds through filters constructed from sorbents and shells and by careful monitoring of water quality.

1.5 Anti pollution methods at sea

Selecting the most suitable method for cleaning up an oil spill is essential and will depend upon the real circumstances of an incident. The volume of spilled oil, the sensitivity of the environment and the availability of the means will dictate the type of spill control strategies deployed. Observation, visually or by use of remote sensing systems, is a vital factor of successful response to marine oil spills. It is used for assessing the location and size of oil contamination and verifying predictions of the movement and fate of oil slicks at marine environment. Containment and recovery of oil using booms and skimmers or adsorbents/ sorbents material, use of chemical dispersants and alternatively in-situ burning and bioremediation, are usually the initial clean up responses to an oil spill at sea (Westermeyer, 1991). These techniques are described in this subchapter.

1.5.1 Containment and recovery

The use of booms to contain and concentrate floating oil prior to its recovery by specialised skimmers or by adsorbents/ sorbents materials is often seen as the ideal solution to a spill since it would remove the oil from the marine environment. Unfortunately, this technique is in direct opposition to the natural tendency of the oil to spread, fragment and disperse under the influence of wind, waves and currents. So, containment and recovery at open sea rarely results in the removal of more than a relatively small proportion of a large spill about 10-15%.

1.5.2 Oil containment by using booms

Booms are used to control the spread of oil, to reduce the likelihood of polluting shorelines and other resources, as well as to concentrate oil in thicker surface layers, making recovery easier (Yang and Liu, 2013). They are made of a floating tube, an immersed skirt, a longitudinal leach and a longitudinal chain. The chain contributes both weight and tension. The leach is generally located on the skirt top. The chain is located on the skirt bottom. Booms are usually moored on the seabed near the shore, a port or an oil terminal but they can also be used at open sea (Muttin, 2008). There are different modes of booms failure, such as entrainment, drainage, critical accumulation, splash-over, submergence, and planning (Goodman et al., 1996).

Booms can be categorized in several types: fence booms with a high freeboard and a flat flotation device, effective in rough water; round or curtain booms with a more circular flotation device and a continuous skirt. They perform well in rough water, but are more difficult to clean and store than fence booms; and non-rigid or inflatable booms that come in many shapes. They are easy to clean and store, perform well in rough seas. Moreover, they are expensive, more complicated to use, puncture and deflate easily.

Finally, there are large booms designed for use in the open sea, usually need cranes and sizeable vessels to handle them; and small, lightweight models designed for manual deployment in harbours and protected waters.

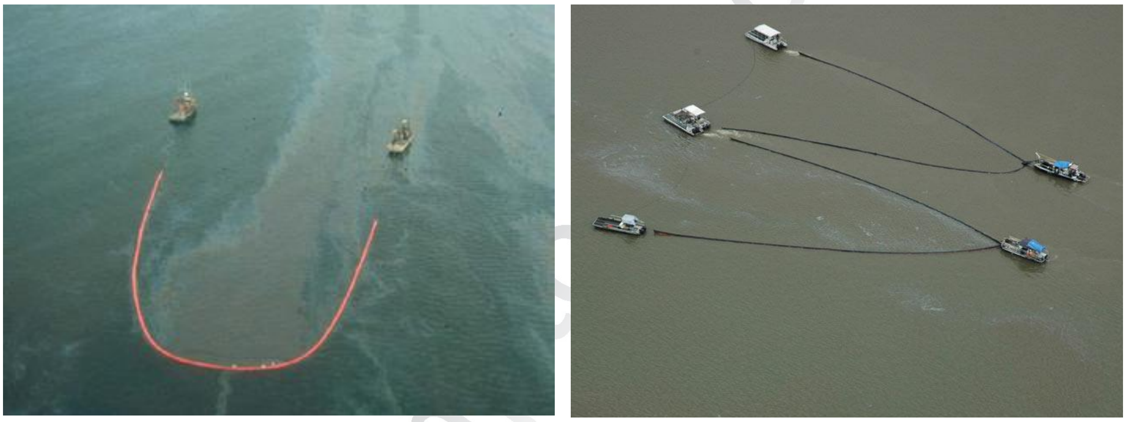


Fig. 1.16 Use of booms at sea in “U” (left) and in “W” (right), configurations, [OSS]

The most important characteristic of a boom is its oil containment, determined by its performance in relation to seawater movement. It should be flexible to conform to wave motion yet sufficiently rigid to retain as much oil as possible. The boom’s characteristic features include the size and design of the freeboard, the height and angle of the skirt, and the momentum of inertia of the boom (Yang and Liu, 2013). Other important boom characteristics are strength, ease and speed of deployment, reliability, weight and cost.

It is essential that a boom is sufficiently robust for its intended purpose and will tolerate inexpert handling, since trained personnel are not always available. Towing booms at sea, for example in “U”, “V”, “J” or “W” configurations, is a difficult task requiring specialised vessels (Fig. 1.16).

1.5.3 Oil recovery by using skimmers

A skimmer is a device for recovering spilled oil from the water's surface, may be self-propelled, used from shore, or operated from vessels. Skimmers incorporate an oil recovery element and some form of flotation. A pump or vacuum device is necessary to transfer recovered oil and water to storage.

As skimmers float on the water surface, strong wind, waves and currents make difficult their use and reduce the effectiveness of most skimmer designs (Ventikos et al., 2004).

Fig. 1.17 Use of skimmers at sea, [OSS]

There is a variety in skimmers design (Fig. 1.17) and a lot of different types that are further described in subchapter 3.3. Skimmer principle, system design and performance, capacity and environmental conditions are factors to be considered in selecting separation technologies for marine oil spill recovery operations (Nordvik et al., 1996).

The intended use and operational conditions should be identified before criteria such as size, robustness and ease of operation, handling and maintenance can be weighed up. At oil terminals and refineries where oil type may be predictable, specialised units may be selected otherwise it is preferable to retain versatility and select units which can deal with a range of oils.

Difficulties posed by floating debris, both natural (sea weeds, sea grasses, trees and branches) and man made (plastic, glass, timber) should be mentioned. Real oil spill case studies reveal that recovery rates reported under test conditions cannot be sustained during a real spill.

1.5.4 Oil recovery by using adsorbents/ sorbents

Sorbents are insoluble materials used to recover liquids through the mechanism of absorption, or adsorption, or both. Adsorbents are insoluble materials that are coated by a liquid on its surface, including pores and capillaries. To be useful in combating oil spills, sorbents need to be both oleophilic and hydrophobic. Although they may be used as the sole cleanup method in small spills, sorbents are most often used to remove final traces of oil, or in areas that cannot be reached by skimmers (Fig. 1.18). Sorbents may be applied to spills manually or mechanically, using blowers or fans.

Fig. 1.18 Use of adsorbents at sea (left), in the port (right), [OSS]

Sorbents can be divided into three basic categories: natural organic, natural inorganic and synthetic (Dryud, 1989). Natural organic sorbents include peat moss, straw, hay, sawdust, ground corncobs, feathers etc. They can adsorb between 3 and 15 times their weight in oil, but there are disadvantages to their use. Some organic of them tend to adsorb water as well as oil, causing the sorbents to sink. Many organic sorbents, like sawdust, are loose particles so it is difficult to collect after they are spread on the water.

Natural inorganic sorbents consist of clay, perlite, vermiculite, glass wool, sand, volcanic ash etc. They can adsorb from 4 to 20 times their weight in oil. They are inexpensive and readily available in large quantities. Synthetic sorbents include man-made materials similar to plastics, such as polyurethane, polyethylene, and polypropylene, are designed to adsorb liquids onto their surfaces, can absorb up 70 times their own weight in oil but are expensive.

1.5.5 The use of chemical dispersants

Dispersants are a group of chemicals specially designed to be sprayed onto oil slicks to accelerate the process of natural dispersion. They are composed of detergent-like surfactants in low toxicity solvents. The dispersants act by emulsifying or breaking up the oil slick into smaller pieces, thus ensuring easy dispersal and/or mixing in aquatic ecosystems (Otitoloju and Popoola, 2009). There are three main types of dispersants: type 1, based on hydrocarbon solvents with between 15-25% surfactant; sprayed neat onto the oil, in dose rates between 1:1 and 1:3 (dispersant: oil); type 2, dilutable concentrate dispersants which are alcohol or glycol solvent based with a higher surfactant concentration in dilution rate 1:10 with sea water; and type 3 with a similar formulation to type 2, designed to be used neat in dose rates between 1:5 and 1:30 (neat dispersant: oil).

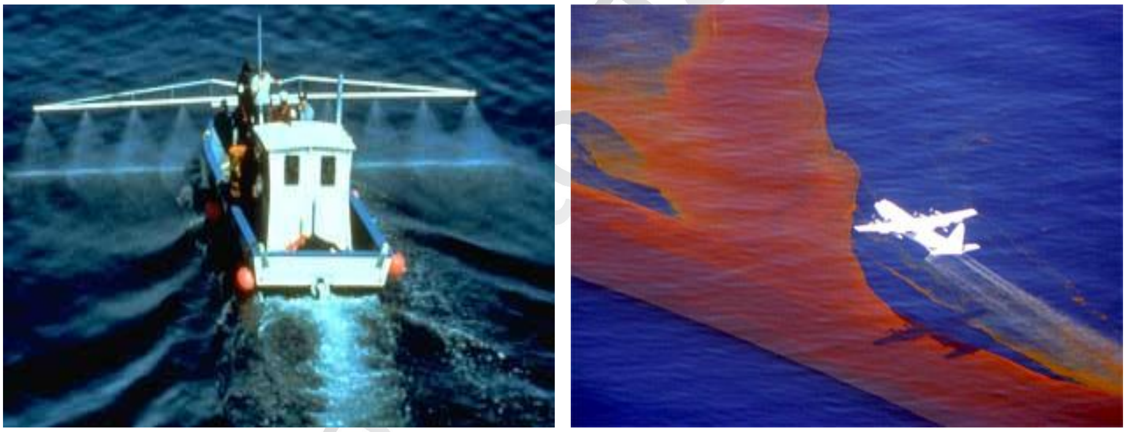


Fig. 1.19 Vessel dispersant spraying (left), aircraft dispersant spraying (right), [OSS]

Dispersants are usually applied from boats equipped with spray arms (Fig. 1.19). Vessels offer advantages for dispersant spraying because they are usually readily available, easy to load and deploy, have cost advantages over aircraft and can apply dispersant fairly accurately to specific areas of a slick (Daling et al., 2002). They also have serious limitations, particularly for larger spills, because of the low treatment rate which they offer and the added difficulty of locating the heaviest concentrations of oil from the bridge of a vessel. The spraying of dispersant from an aircraft (Fig. 1.19) or a helicopter has the significant advantages of rapid response, good visibility, high treatment rates and optimum dispersant use (Daling et al., 2002).

In addition, aerial means allow treatment of spills at greater distances from the shore than with vessels. Nevertheless, the aerial spraying of dispersant has also serious limitations, particularly the high operational cost, the need of sunlight existence and the low wind speed as the aircrafts operate only daily and in low altitude where strong winds make difficult the clean-up operation.

When used appropriately, dispersants can be an effective method of response to an oil spill. They are capable of rapidly removing large amounts of certain oil types from the sea surface by transferring it into the water column. They can also delay the formation of persistent water-in-oil emulsions and promote the biodegradation of oil in the water column (Fingas, 2011b). The use of dispersants has limitations and their use should be carefully planned and controlled. In the open sea, dispersed oil concentrations after spraying are unlikely to remain high for more than a few hours and significant biological effects are therefore improbable. In shallow waters close to the shore, where water exchange is poor, higher concentrations may persist for long periods and may give rise to adverse effects. Many factors influence dispersant effectiveness, including oil composition, sea energy, state of oil weathering, type of dispersant used and the amount applied temperature, and salinity of the water (Fingas, 2011b). Dispersant use will also depend upon national regulations governing the use of these products.

Alternative techniques

The use of booms and skimmers to recover floating oil and dispersants to enhance natural dispersion are well established methods of responding to oil spills. However, alternative techniques have been promoted including in-situ burning and bioremediation.

1.5.6 In-Situ Burning

In-situ burning is the term given to the process of burning oil slicks at sea, at or close to the site of a spill (Fig. 1.20). Burning may be seen as a simple method which has the potential to eliminate large amounts of oil from the sea surface. In reality, there are a number of problems which limit the feasibility of this response technique. These include: the ignition of the oil; maintaining combustion of the oil slick; the production of large quantities of smoke; the distance of the oil from a populated area; the formation and sinking of viscous - dense residues (Buist et al., 1994).

Fire proof containment boom and an ignitor will most probably be required for a burn to be undertaken. Although crude oils will burn easily, light and medium oils are generally more difficult to ignite once they have lost in excess of 20% by weight. Ignition and any consequent burning are further hindered by the formation of oil-in-water emulsions and by the fragmentation and scattering of the oil slick over a wide area by winds and currents (Potter and Buist, 2008).

Fig. 1.20 In situ burning at sea, [OSS]

For a successful in-situ burn the layer of oil on the water surface needs to be at least 2-3 mm thick to counter the cooling effect of the wind and sea. The state of the sea can limit the achievement of any burn. Short, steep waves will reduce the efficiency of the burn and choppy seas may extinguish the fire altogether. Once alight, the slick itself needs to reach sufficiently high temperatures to keep the fire burning (Buist et al., 1994). As a result of some of these difficulties, a significant quantity of oil may remain unburned at sea.

1.5.7 Bioremediation

Oil is biodegraded over a period of time into simple compounds such as carbon dioxide, water and biomass. Bioremediation describes a variety of processes which can be used to accelerate natural biodegradation. In particular bio-stimulation is the application of nutrients, and bio-augmentation is the addition of microbes specially selected to degrade oil. Even though the idea of bioremediation is attractive, its practical use is restricted. More specifically, bioremediation should not be used on the sea surface since any materials added are likely to be rapidly diluted and lost from the slick. Although bioremediation may improve the rate of degradation of floating slicks (Pritchard and Costa, 1991) the procedure is still too slow to prevent the vast majority of the oil reaching the shoreline.

Use of bioremediation on the shoreline is more controversial as the same level of control is unfeasible to obtain in the marine environment. This process is therefore not suitable for removing large amounts of oil and should only be considered where the concentration of oil is low as a final polishing technique (Pritchard et al., 1992). In any case, the capability of bioremediation is limited as some of the more complex components of the oil, as resins and asphaltenes, may remain partially or totally undegraded.

1.6 Shoreline clean-up and disposal of oily waste after recovery

Given the difficulties of cleaning up oil at sea, many oil spills result in contamination of shorelines. The oil which reaches the coast generally has the greatest environmental and economic impact and determines to a large extent the political and public perception of the scale of the incident, as well as the costs.

1.6.1 Shoreline clean up

There are a variety of options for the treatment and cleanup of oiled shorelines. Some techniques, such as washing or manual removal, remove and recover the oil or oiled material. It is important to start removing oil promptly from contaminated shorelines because as time passes and the oil weathers, it will stick steadily to rocks and sea walls (Sergy et al., 2003). Shoreline clean-up does not usually require specialised equipment and takes account of the characteristics of the oil, the level of contamination and the relative environmental, economic and amenity sensitivities of different locations.

Shoreline clean-up (Fig. 1.21) is usually carried out in stages, starting with the removal of the heaviest accumulations of oil. The need for secondary cleaning and the degree to which it is carried out must be judged against the use of the shoreline and economic and environmental sensitivities. In many instances natural degradation processes deal with them quickly and effectively, especially where wave action and tidal water movements are strong. Temporary storage of recovered oil before it is moved for disposal must be also considered.

Fig. 1.21 Shoreline clean-up’s operations, [OSS]

Bulk oil can easily be removed from sand beaches, using a combination of manual labourers assisted by front-end loaders and other mechanical equipment to transport recovered residues. Cleaning of rocky shores close to amenity beaches or sea walls is normally straightforward. Oil can be recovered manually or by using vacuum units or other skimmers. Low pressure flushing with sea water may also be employed to wash oil wastes to collection points. Final cleaning usually requires high pressure flushing, high pressure hot water washing or even sand blasting. Leaving residual oil to weather and degrade naturally is usually recommended for sensitive shoreline types such as salt marshes and mangroves, because they have been shown to be more easily damaged by the physical disturbance caused by clean-up teams and vehicles than by the oil itself (Prince, 1998).

1.6.2 Disposal of oily waste after recovery

Recovery of spilled oil, either from the sea surface or from the shoreline frequently results in mixing of collected oil with seawater, debris and beach material. So the volume of oily waste, for treatment and disposal, is increased. Ideally the collected oil should be reprocessed through an oil refinery or recycling plant. Unluckily this is not often possible as the oil may have weathered or been contaminated with debris and seawater. Various methods of disposal are available including direct disposal to controlled landfill sites and destruction by incineration or biological processes (Sergy et al., 2003). The disposal method chosen (Fig. 1.22) will depend on a number of factors including the amount and type of oil collected the location of the spill, the likely costs involved and environmental, legal or practical limitations.

Direct disposal of oily solid waste, mixed with domestic rubbish, to designated landfill sites is a commonly used disposal method, however in some countries (e.g. EU States) waste pre-treatment may be required. Modern sites are usually enclosed by an impermeable membrane to prevent substances from leaching from the site but, provided the waste is properly mixed with the domestic refuse, there is little risk of oil leaching from the site.

Fig. 1.22 Disposal of oily waste, [OSS]

As a waste disposal option incineration has the major advantage of substantial volume reduction of waste. This is increasingly important due to the diminishing space available for disposal by landfill (Wheatley and Sadhra, 2004). When oil is first spilt it is a flammable material. In a few hours it loses any volatile components and picks up a high proportion of water making the oil’s burning very difficult. This can be overcome by using an incinerator which contains the waste to be burnt and generates the high temperatures necessary for total combustion. The applicability of incineration depends largely on local legislation, environmental conditions and estimated costs.

Oil and oily wastes are broken down by biological processes. Biodegradation of oil by micro-organisms only takes place at the oil-water interface so that the oil must be first mixed with a moist substrate. The rate of biodegradation could be increased by the application of soluble and slow release fertilizers. Attempts to use these products in actual spill situations have met with very little success (Owens et al., 2003) mainly due to the oil concentrations being too high and the difficulty in maintaining required nutrient levels.

CHAPTER 2
MARINE ENVIRONMENT PROTECTION IN GREECE

2.1 Introduction

Europe is the world’s largest market in crude oil imparts, representing about on third of the world total. The sea is a basic resource and a key measure of the quality of life for all Mediterranean countries. The semi-enclosed Mediterranean Sea covers about 2.5 million km^2, and its coastal zone is habitated by some 81 million people expected to increase to as many as 170 million by 2025 (U.N. Statistical Office, 1993). Due to the region’s mild climate and historical background, the annual number of tourists is estimated to reach 260 million by 2025.

Greek economy depends mostly on tourism and fishing; these activities depend directly on water quality. It is thus obvious that protection of the marine environment is of great importance to the country, ensued from European Directives and National Decrees (Table 2.1), with special emphasis on the Mediterranean environment.

2.2 Structure of Greek National Contingency Plan

2.2.1 Description

Pursuant to the Greek National Contingency Plan (GNCP), the Marine Environment Protection Division (MEPD) of the Ministry of Shipping, Maritime Affairs and the Aegean (MSMAA), staffed both by officers of the Hellenic Coast Guard (HCG) and by civil personnel, is the competent authority for combating marine pollution incidents. Local Port Authority coordinates the response, for a small spill. It is only in the case of a larger spill that the MEPD will assume control of and will dispatch supplementary means and equipment in order to assist the local authorities of the affected area.

Private resources belonging to onshore installations, ships or to antipollution contractors are also used under the supervision of the competent Authority. In the case of spills of unknown origin, clean up is carried out by the HCG, whereas coastline clean up is carried out by the municipal Authorities.

Table 2.1 National and International legislation valid in Greece on the protection of the marine environment

International legislation	National legislation
LONDON 1972: International Convention on the dumping of wastes and other matters.	E1b/221/1965: Public Health Regulation.
BARCELONA 1976: International Convention on the Protection of Mediterranean Sea against Pollution.	Legislative decree 187/1973: Code of Public Maritime Law.
MARPOL 1973/78: International Convention on the Prevention of Pollution from ships.	Law 1650/1986: Environment Protection.
HELLAS-ITALY Bilateral Agreement on the protection of the Ionian Sea, 1978.	Presidential decree 55/98: Protection of the marine environment (ex Law 743/77).
OPRC 1990: International Convention on Oil Pollution Preparedness, Response and Cooperation.	Presidential decree 11/2002: National Contingency Plan.
CLC 1992: International Convention on Civil Liability for Oil Pollution Damage.	Law 3100/2003: Ratification of the Protocol for the readiness, collaboration and coping with incidents of sea pollution by dangerous and harmful substances, 2000.
FUND 1992: International Convention on the Establishment of an International Fund for Compensation for Oil Pollution Damage, 1992.	Law 3104/2003: Ratification of the 1997 Protocol modifying the International Convention for the Prevention of Pollution from the 1973 Ships, as modified by the 1978 Protocol being related to it.
International Convention for the civil responsibility for the damage of pollution from petrol for vehicles, (Bunkers Convention), 2001.	Presidential degree 82/2004: Substitution of 98012/2001/1996 common Prefectural Decision “Definition of the measures and the terms for the management of the used mineral oils. Measures, terms and programme for the alternative use of the Waste Lubricant Oils”.
International Convention for the inspection of harmful systems of the ships’ hull painting, (AFS Convention), 2001.	Presidential degree 3/2005: Modification of the provisions under which the Greek Legislation was adapted in accordance with other equivalent EU Instructions in regard to the security in navigation and the prevention of pollution by ships in compliance with the Instruction 2002/84 EK of the Committee of the 5th November 2002.
Ratification of the Agreement between the Ministry of Environment, Land Planning and Public Works of Greek Democracy and the Ministry of Environment and Water of the Democracy of Bulgaria about the collaboration in the field of environmental protection, 2005.	Prefectural Decisions (relating to the subject).
Ratification of the Memorandum of Understanding and Collaboration in the field of environmental protection between the Ministry of Environment, Land Planning and Public Works of Greek Democracy and the Ministry of Environment of the Democracy of Albania, 2005.	Port Police Regulations.
European Union Regulations and Directives related to the marine environment.	

2.2.2 Regional pollution combating centers

In areas where pollution incidents occurred on several occasions, as well as in areas near facilities (oil refineries, storage companies, oil products and noxious substances trading companies, shipyards, ship repair industries, land waste reception facilities, industries and manufactures of all kinds established at sea, coastal areas or inland using the sea and the coastline in a direct or indirect way or adversely affect in a direct or indirect way the marine environment), the MSMAA establishes Regional Pollution Combating Centers (RPCCs). These centers (Fig. 2.1) are part of Port Police Departments, founded by the MSMAA in the following Greek ports: Piraeus, Elefsis, Kavala, Thesaloniki, Patra, Chania, Isthmia, Syros, Neapolis Vion, Volos, Pilos, Alexandroupolis, Limnos, Chios and Rhodes. Igoumenitsa, Preveza, Zakinthos, Corfu, Iraklio, Mitilini, Lavrio, Santorini, and Samos established as RPCCs by the Presidential Decrees 63 and 64/2004. The RPCCs are staffed with experienced personnel and are properly equipped in order to respond immediately and, thereby, control effectively any marine pollution incident, given that time is a crucial factor.

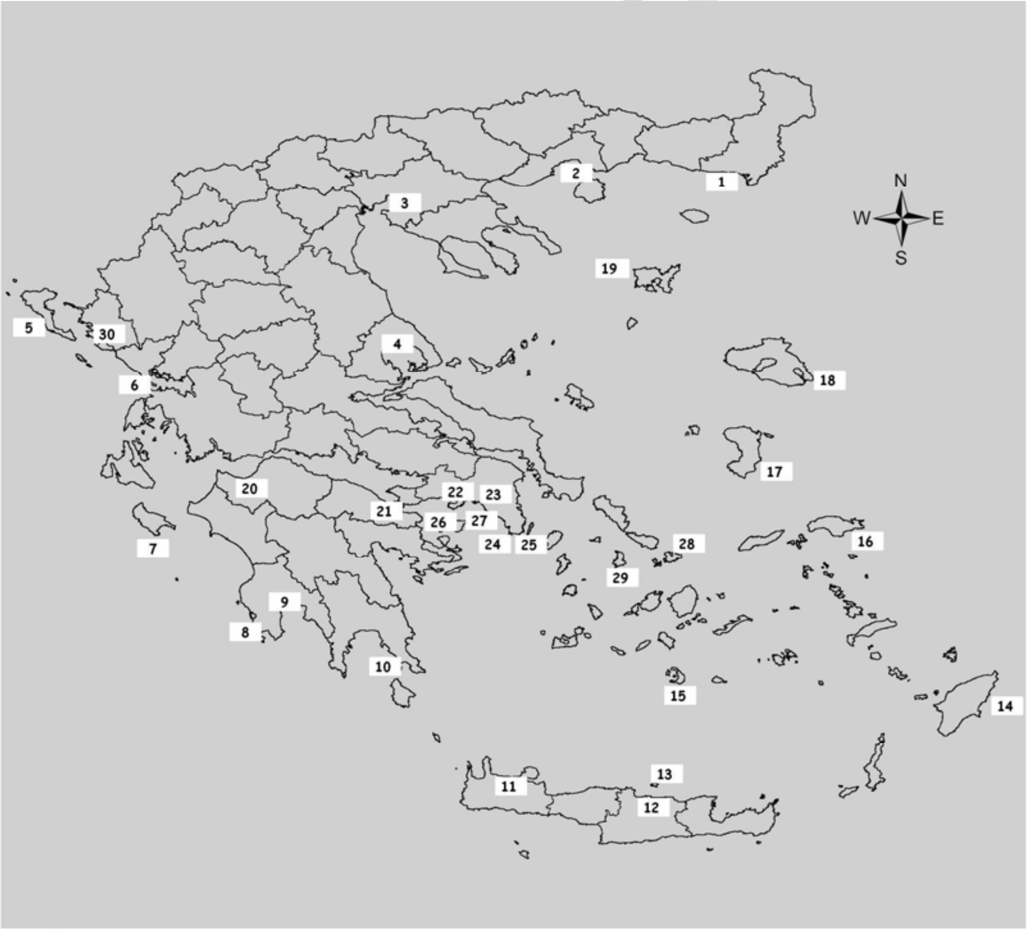


Fig. 2.1 The Regional Pollution Combating Centers network (1: Alexandroupolis, 2: Kavalla, 3: Thessaloniki, 4: Volos, 5: Corfu, 6: Preveza, 7: Zakinthos, 8: Pilos, 9: Kalamata, 10: Neapolis Vion, 11: Chania, 12: Iraklion, 13: Dia, 14: Rhodes, 15: Santorin, 16: Samos, 17: Chios, 18: Mitilini, 19: Limnos, 20: Patra, 21: Isthmia, 22: Elefsina, 23: Piraeus, 24: Lavrio, 25: Cavo Doro, 26: Aegina, 27: Glyfada, 28: Mykonos, 29: Syros, 30: Igoumenitsa)

2.3 Greek National Contingency Plan response mechanism

2.3.1 Oil spill response mechanism

The GNCP covers the whole of the territory, while the Local Contingency Plan (LCP) refers to the Port Authority's specific geographical domain of responsibility. The Port Contingency Plan (PCP) is the contingency plan, as approved, of the party responsible for the administration or operation of the port. The Facility Contingency Plan (FCP) is the contingency plan, as approved, of the coastal or offshore oil handling or exploitation installation, while the Regional Contingency Plan (RCP) is the regional contingency plan, which constitutes a combination of the local plans of the Port Authorities involved under the general command of the hierarchically superior Local On-Scene Commander.

The GNCP designates the Marine Rescue Coordination Center (MRCC) of the MSMAA in cooperation with the MEPD as the National Coordinator and provides for the escalation of the response actions depending upon the significance of each pollution incident (Fig. 2.2). A three-tiered activation of the response mechanisms is adopted for combating marine pollution incidents caused by oil (Table 2.2), on the basis of the quantity of oil spilled; the quantity of 700 tn of oil escaped in tiers 2 and 3 represents the upper limit for activating the first two levels.

Table 2.2 The three - tiered activation of the response mechanisms adopted for combating marine pollution incidents caused by oil [MSMAA]

Tier	Refers to	Implemented Plan	Quantity of escaped into the environment
1	response planning for operational or accidental pollution, which invariably should be, treated the current capabilities of each facility or commercial port	PCP/ FCP/ LCP	< 7 tn
2	response planning for pollution incidents, whose significance extent the coordination of more sources to provide response technical means, equipment and personnel	LCP/ RCP/GNCP	7-700 tn
3	large-scale serious pollution incidents when all available resources are placed in readiness and the existing potential for pollution fighting is activated on a national scale	GNCP	>700 tn

Nevertheless, in practice, decision making on pursuing activities also takes into account the prevailing conditions during the outbreak of the incident and the well-founded prediction of its development in conjunction with the estimated subsequent effects.

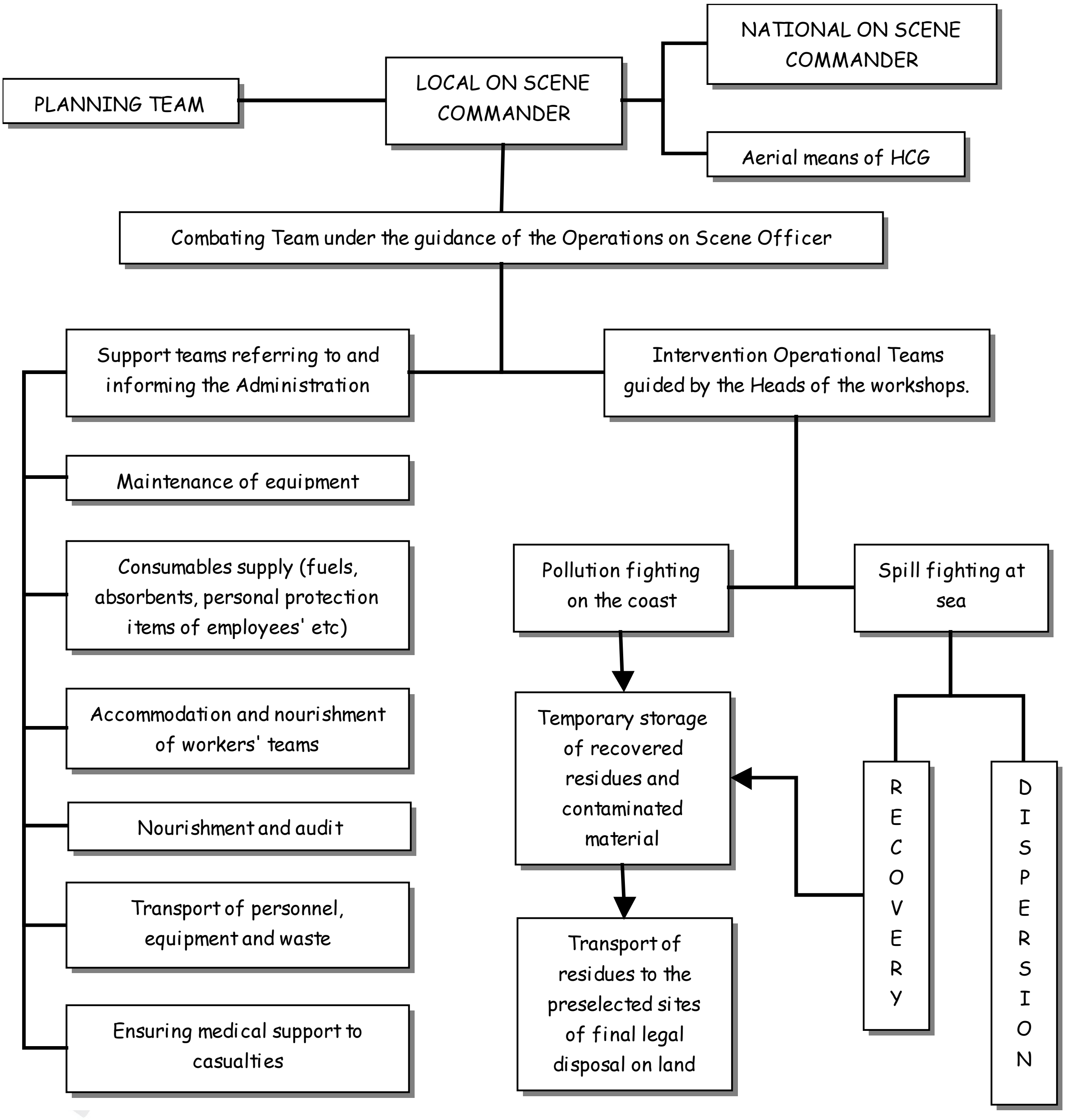


Fig. 2.2 Greek National Contingency Plan for marine pollution incidents [MSMAA]

2.3.2 Contribution of the involved Services

The GNCP is supported by the following involved Services: Ministry of Environment, Physical Planning and Public works, Ministry of National Defense / General Staff, Ministry of National Economy, Ministry of Foreign Affairs, Ministry of Transport & Communication, Ministry of Interior Affairs / General Secretariat of Civil Protection, Ministry of Public Order, Ministry of Health and Social Security, Ministry of Agricultural, Prefectures and Local Authority Organizations, National Weather Service, Hellenic Hydrographical Service and Port Organizations.

Table 2.3 Contribution of Services involved in the handling of marine pollution incidents

Authority/Service/ Agent	Short description of contribution
Ministry of Environment, Physical Planning and Public works.	Assists with specialized personnel means in combating coast pollution.
Ministry of National Defense/ General Staff.	Locates / Surveys pollution incidents and assists in marine pollution combat.
Ministry of National Economy.	Provides administrative support through Custom Authorities.
Ministry of Foreign Affairs.	Informs the Diplomatic State Authorities involved in pollution incidents.
Ministry of Transport & Communication.	Assists with specialized personnel - means in combating coast pollution.
Ministry of Interior Affairs/ Secretariat of Civil Protection.	Activates General Secretariat Civil Protection mechanism for the combating coast pollution.
Ministry of Public Order.	Assists in coast antipollution through Hellenic Police – Fire Brigade.
Ministry of Health and Social Security.	Takes emergency measures to eliminate the unfavorable consequences of pollution incident to Public Health.
Ministry of Agricultural.	Takes measures regarding fishing – water agriculture.
Prefectures and Local Authority Organizations.	Assist in coast cleaning in case of pollution.
National Weather Service.	Issues regular weather forecast.
Hellenic Hydrographical Service.	Issues special directives for seamen in polluted areas.
Port Organizations and Port Pay Offices.	Activate PCP in case of port pollution / provide waste reception facilities.
Hellenic Centre for Marine Research.	Provides scientific support for combating marine pollution incidents at sea and coasts.
State Chemical Laboratory.	Chemically identifies the pollutants / Defines the allowed types of chemical dispersants.
Research Institute "Demokritos"	Provides directives to National Coordinator in case of radioactive residues.
Oil refineries - oil companies.	Activate FCP / Assist with personnel – means in coast antipollution.
Antipollution contractors.	Take over / Assist in sea – coast antipollution.
Port facilities contractors.	Assist to the handling – storage of collected residues.
Tugboat and rescue boat installations.	Assist in ships – cargoes rescue.
Shipyards and ship-repair installations.	Activate FCP / Assist with personnel – means in coast antipollution.
Various volunteers.	Assists in sea – coast antipollution.

Furthermore, GNCP is supported by the following Services: Hellenic Centre for Marine Research, State Chemical Laboratory, faculties and Research Institutes (e.g., "Demokritos", Maritime Biology Research Institute of Crete, etc), oil refineries - oil companies, antipollution contractors, port facilities contractors, tugboat and rescue boat companies, shipyards and ship-repair installations, various volunteers. The contribution of the Services involved in combating marine pollution incidents is shown in Table 2.3.

2.4 Weak points of Greek National Contingency Plan

Thorough analysis of real incidents occurred in Hellenic sea area: cargo vessel “Sigulda” and tanker “Geroi Chernomorvia” (03-05-1992); tanker “Iliad” (09-10-1993); cargo vessels “Antigonos” and “Container Zim Pacific” (03-09-1996); cargo vessel “Nordland” (29-08-2000); cargo vessel “Eurobulker X” (01-09-2000), has revealed several drawbacks of the GNCP, in both design and implementation:

- Distribution of responsibilities to many Services - inability of Services involved cooperating (Liu and Wirtz, 2005).
- Lack of specific marine pollution hypothetical incident scenarios of “what if…if then” type with already planned ways of dealing with them.
- Incomplete analysis of other strategies-alternatives.
- No real time response.
- No procedure for the detection of unknown pollution offender is used.
- New technologies are not used to the limit of their possibilities:
- No satellite system for detection and monitoring of oil spill (Jones and Mitchelson–Jacob, 1998), or other pollution form is used.
- Operators dealing with marine pollution do not use data bases which give them in real time access to oceanographic hydrographical, weather and climate data, or data on wave movement, wind direction and force, seabed situation etc or other local particularities and other information based on statistical historical data of great usefulness in handling marine pollution incidents.

- No computer systems or statistical-mathematical models are used in simulation environment (Reed et al., 1995) that may assist a lot in foreseeing the development of a marine pollution incident.

2.5 Oil pollution statistics in Greece

In this subchapter statistics about sea pollution incidents happened in Greece, mainly in 2013, are described and analyzed.

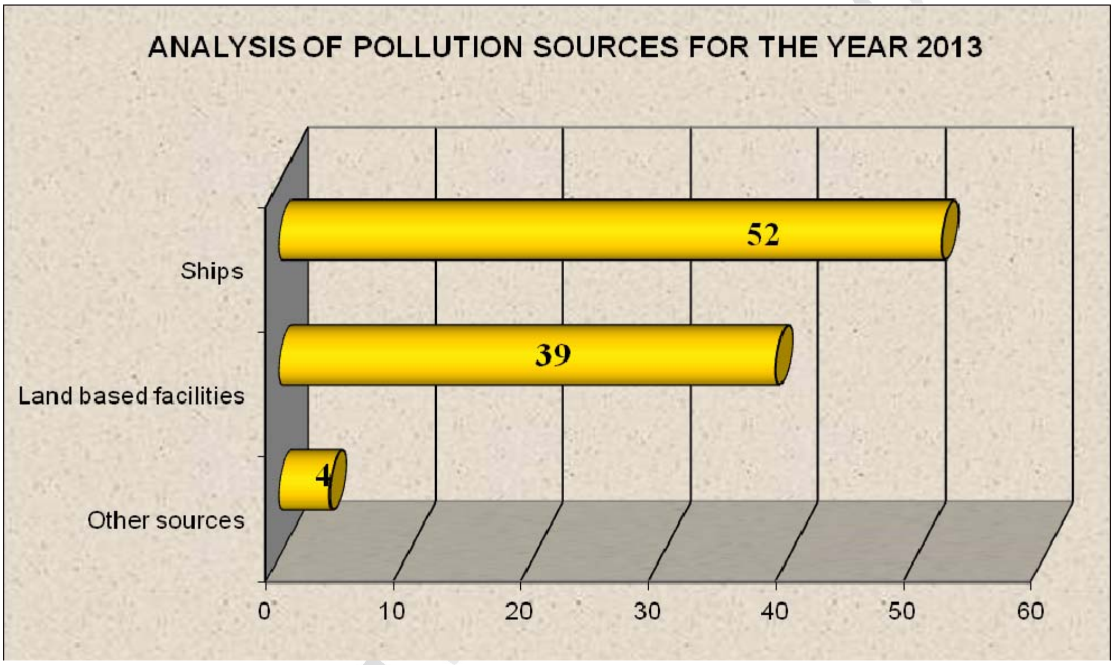


Fig. 2.3 Analysis of pollution sources, 2013 [MSMAA]

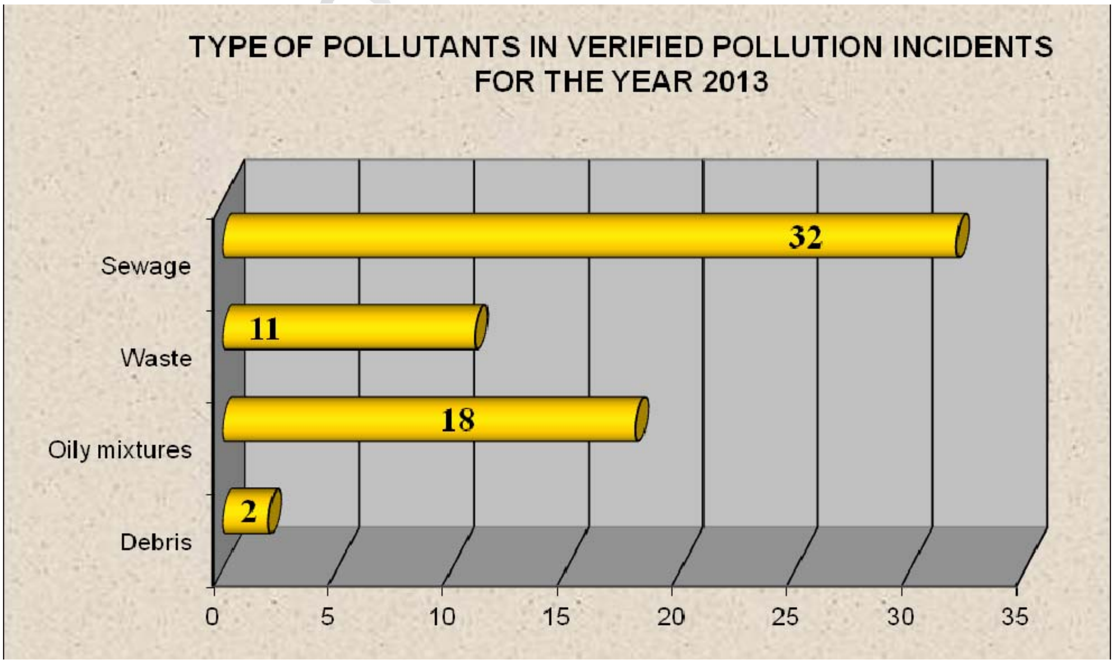


Fig. 2.4 Analysis of the type of contaminants in pollution incidents, 2013 [MSMAA]

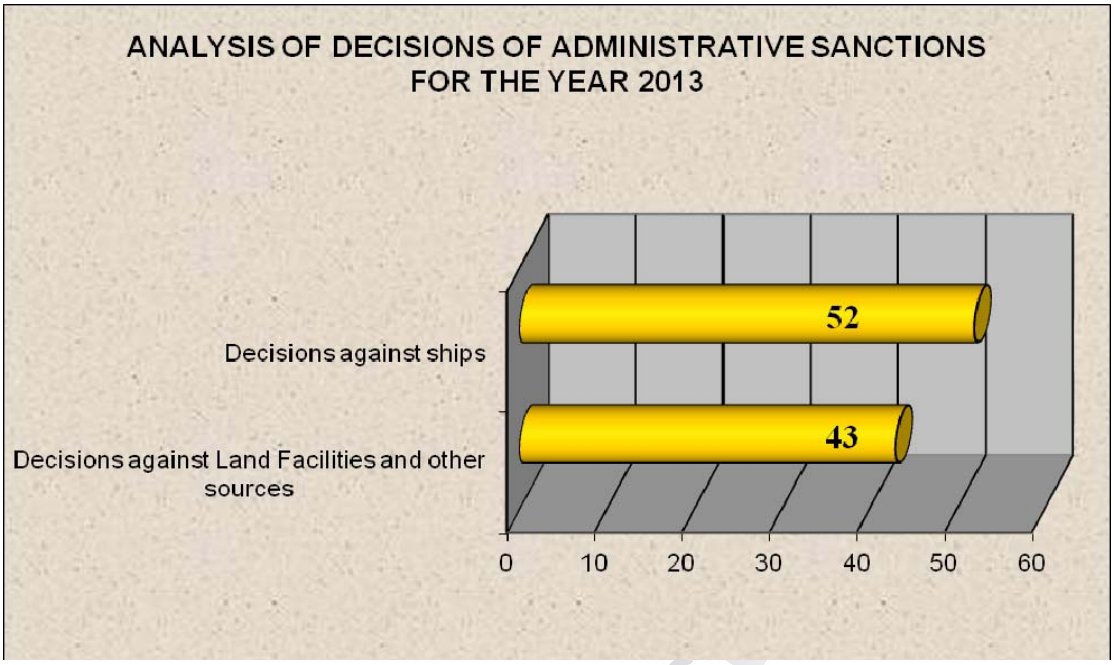


Fig. 2.5 Analysis of Decisions of administrative sanctions based on the pollution source, 2013 [MSMAA]

A division of the Decisions of administrative sanctions in relation to the source of the pollution (ships/ land facilities or other sources) is presented in Fig. 2.5, for 2013, while in Fig. 2.6 the total amount of the imposed fines for Marine Environment Protection Issues, based on the applied legislation for the same year is performed.

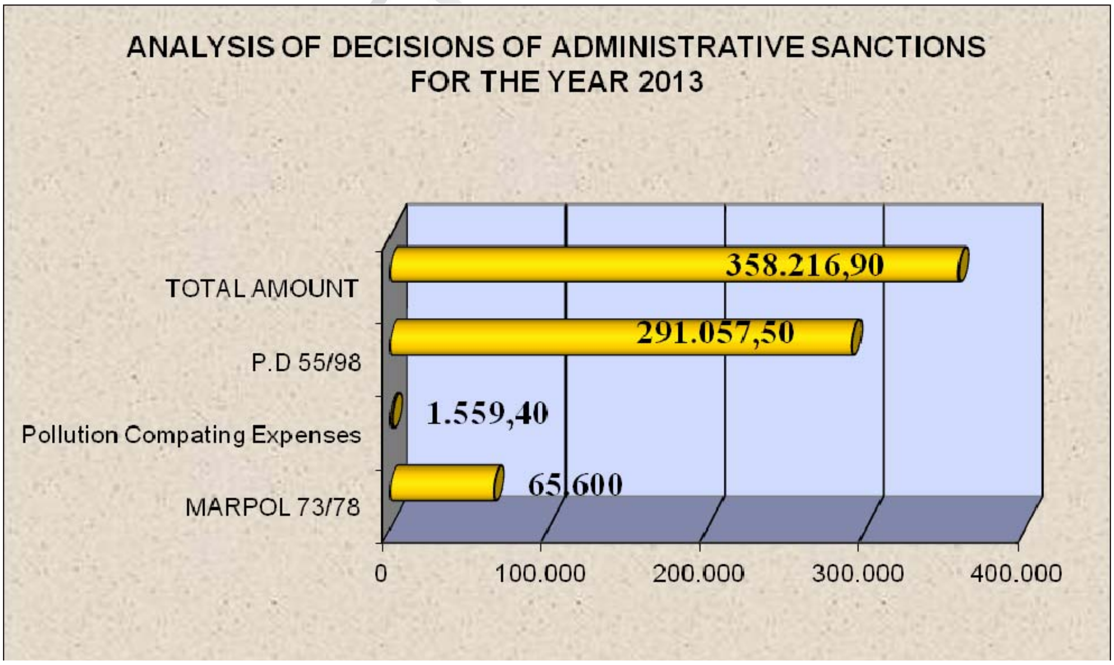


Fig. 2.6 Total amount of imposed fines for Marine Environment Protection Issues, 2013 [MSMAA]

Finally, in Table 2.4 we see the imposed administrative sanctions to ships/ land facilities and other sources for violations of Marine Environment Protection Issues from 1984 to 2012.

Table 2.4 Imposed administrative sanctions to ships – land facilities and other sources for violations of Marine Environment Protection Issues, 1984 – 2012 [MSMAA]

Year	Ships		Land Facilities - Other sources		Ascription Expenses		Total Amounts	
	Number of Decisions	Amount in Drachmas/€	Number of Decisions	Amount in Drachmas/€	Number of Decisions	Total amount	Total of Decisions	Amounts in Drachmas/€
1984	193	15,342,000	177	28,115,000			370	43,457,000
1985	192	19,816,000	155	24,241,000			347	44,057,000
1986	158	28,588,000	215	26,228,000			373	54,816,000
1987	124	17,615,000	141	16,080,000			265	33,695,000
1988	99	14,667,000	184	20,110,000			283	34,770,000
1989	138	17,590,000	131	16,483,000			269	34,073,000
1990	218	505,627,000	158	48,425,000			376	554,052,000
1991	288	198,180,000	98	40,095,000			386	238,275,000
1992	273	519,134,427	199	45,600,000			472	564,734,427
1993	168	271,535,000	152	114,740,000			320	386,275,000
1994	221	455,645,000	112	25,690,000			333	481,335,000
1995	359	470,414,083	146	49,925,000			505	520,332,083
1996	278	690,109,284	140	71,910,000			418	762,019,284
1997	405	387,710,000	189	36,970,000			594	424,680,000
1998	200	203,573,216	141	77,260,000			341	280,833,216
1999	147	242,676,559	151	67,790,000			298	310,466,559
2000	182	602,165,015	198	133,650,000			380	735,815,015
2001	180	3,096,105 €	252	474,571 €			432	3,570,676 €
2002	190	989,737 €	183	391,515 €			373	1,381,252 €
2003	242	670,323 €	175	311,514 €			417	981,837 €
2004	71	206,722 €	74	161,610 €			145	368,332 €
2005	119	---	130	---			249	872,286 €
2006	184	---	161	---			345	832,195 €
2007	348	3,069,632 €	141	245,000 €			489	3,314,632 €
2008	516	4,080,194 €	109	154,100 €	16	821,856 €	641	5,056,150 €
2009	196	1,278,006 €	103	268,100 €	10	216,346 €	309	1,762,452 €
2010	81	397,700 €	81	151,900 €	11	95,956 €	173	645,556 €
2011	79	265,390 €	101	156,600 €	08	211,888 €	188	633,878 €
2012	77	328,457 €	39	37,550 €	07	305,715 €	123	671,722 €

CHAPTER 3
THE PROPOSED NATIONAL CONTINGENCY PLAN

3.1 Methodology

Whilst the technical aspects of combating an oil spill in the marine environment are clearly important, the effectiveness of the response to a major pollution event will ultimately depend on the quality of the contingency plan and of the organisation and control of the various aspects of the clean-up operation.

The Proposed National Contingency Plan (PNCP), in this study determines as the competent authority for combating marine pollution incidents in Greece the Ministry of Shipping, Maritime Affairs and the Aegean (MSMAA). For the needs of the PNCP, a methodological framework under the form of an algorithmic procedure was developed, consists of 18 activity stages and 8 decision nodes, covers an hypothetical event, of either a vessel in danger (with or without an oil leakage) or an oil spill appearance without identifying the source of marine pollution, from the beginning to its efficient handling, (for their interconnection see the flowchart in Fig. 3.1).

The "heart" of this contingency plan includes a multi-criteria analysis mechanism which is defined from 9 to 14 activity stages in the flowchart (Fig. 3.1) and is totally supported by a software system tool created by Dr. Athanasios Batzias. The alternative anti-pollution methods that are proposed by the PNCP are: in-situ burning, oil recovery by using oil skimmers, oil recovery by using oil adsorbents/ sorbents, oil containment by using oil booms and use of chemical dispersants.

Linguistic variables were formed, categorized and analyzed by experts in oil spill fields for each one of the above mentioned alternatives. These linguistic variables include data like the distance of the incident from populated, touristy or ecologically sensitive areas; the type of the sea area, the water salinity, the depth of the water and the possible sea currents; the quantity and the characteristics of the spilled oil like oil thickness and viscosity; and finally the weather prevailing conditions like the speed of the wind and the height of the waves.

The alternative oil combating methods are expressed via Rules Index (RI) that are depended on the linguistic variables concerning each method. Rules Index that deal with the selection of the suitable way to combat oil pollution are also considered while an oil spill anti-pollution method has already been used.

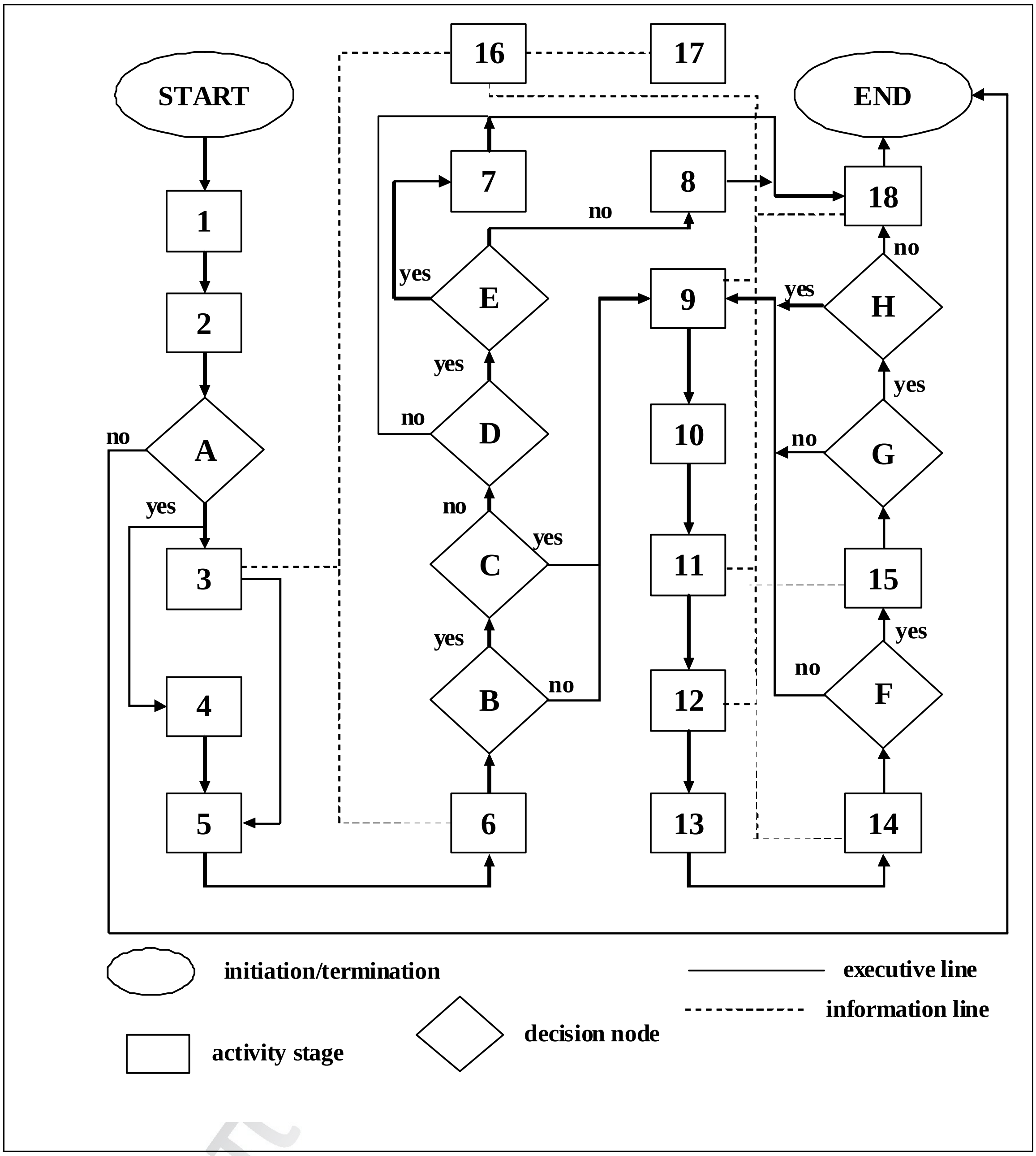


Fig. 3.1 The methodological flowchart of the PNCP

1. Early warning about an event of either a vessel in danger (with or without an oil leakage) or an oil spill appearance without identifying the source of marine pollution.

2. Attempt to confirm the event.

A. Is the event confirmed?

3. Activities for setting all responsible authorities in alarm condition.

4. Information retrieval/ selection concerning meteorological/ sea conditions and vessel/ cargo details.

5. In-situ examination of the event for gathering characteristic details at the required information regularity.
6. Evaluation of information gathered/ selected.
B. Has the vessel responsible for (possible) oil leakage been identified?
C. Is there observed oil leakage?
D. Is there possibility of oil leakage?
E. Is the vessel feasible to be towed or moved by its own means?
7. Towage of the vessel or movement by its own means to a safe port with proper facilities.
8. Repair, pump.
9. Selection of information for performing MCA.
10. Estimation of the Rules Index.
11. Assignment of weight values w_i to the elements of the linguistic variables vector (i=1,2,…,n; where n is the number of the linguistic variables under consideration).
12. Assignment of grades a_{ij} to the alternative methods preference matrix (i=1,2,…,n; j=1,2,…,m; where n is the number of the linguistic variables and m is the number of the methods under consideration).
13. Performance of MCA.
14. Sensitivity analysis of the alternative solution ranked first in descending order of preference.
F. Is this alternative solution sensitive?
15. Implementation of the proposed solution.
G. Is the implementation satisfactory?
16. Surveillance.
17. Searching in external KBs for data mining by means of an Intelligent Agent, according to Batzias and Marcoulaki, (2002).
18. Development/operation/enrichment/updating of an internal Knowledge Base (KB)
H. Is there another (set of) antipollution alternative(s) available?

3.2 Linguistic variables of combating oil pollution methods

In subsection 1.5, the basic anti-pollution methods of oil spills were performed. In this subsection the above mentioned methods will be connected with their linguistic variables in order to express via Rules Index the use of these methods.

The linguistic variables were formed, categorized and analyzed by experts in oil spill fields.

3.2.1 In–situ burning

In-Situ Burning, (ISB), involves controlled burning of oil that has spilled from a vessel or a facility, at the location of the spill. The Torrey Canyon incident (1967) in Great Britain was the first major oil spill in which burning was attempted (Walton and Jason, 1999). Due to the emulsification of the oil, results were unsuccessful. One successful burn could be mentioned, conducted during the Exxon Valdez (1989) oil spill (Alaska Oil Spill Commission, 1990).

In case of the New Carissa (1999) the conditions were favourable for burning (U.S. Coast Guard, 1999). The total amount of oil that was burned is estimated to be between 165,000 – 255,000 gallons. Despite its drawbacks, ISB may be an efficient cleanup method (ITOPF), under certain conditions where there are few negative effects on humans or the environment. These conditions include remote areas, areas with herbaceous or dormant vegetation, and water or land covered with snow or ice.

Table 3.1 Linguistic variables for the case of in-situ burning

Linguistic variables	Categorization		
	Low (L)	Medium (M)	High (H)
Distance from populated, touristy or ecologically sensitive areas (DFA), in km	0 - 1.3 - 2.6	2.0 - 3.2 - 5.0	3.5 - 6.5 - 8.0
Oil Thickness (OT), in mm	0 - 2.4 - 3.9	3.0 - 5.3 - 8.0	5.6 - 9.3 - 12.0
Wind Speed (WS), in knots	0 - 5 - 13	10 - 16 - 23	17 - 30 - 50
Waves Height (WH), in m	0 - 0.15 - 0.4	0.3 - 0.73 - 1.0	0.75 - 1.2 - 3.0

The main Linguistic Variables concerning ISB were formed by experts in oil spill fields, from researching on the literature survey (Fingas and Laroche, 1991; Evans et al., 1991; Williams and Cooke, 1985; Evans et al., 1990) and studying the relevant ASTM Standards (F625, 2000; F1788, 2003). In Table 3.1 these Linguistic Variables for the case of in-situ burning as oil anti-pollution method are presented.

3.2.2 Oil recovery by using oil skimmers

Oil skimmers are devices, which can be used to recover floating oil from the surface of water. The main Linguistic Variables concerning oil recovery using oil skimmers were formed by experts in oil spill fields, from researching on the literature survey (Ventikos et al., 2004; Nordvik et al., 1996) and studying the relevant ASTM

Standards (F625, 2000; F1778, 2002). In Table 3.2 these Linguistic Variables for the case of oil recovery by using oil skimmers as oil anti-pollution method are presented.

Table 3.2 Linguistic variables for the case of oil recovery by using oil skimmers

Linguistic variables	Categorization		
	Low (L)	Medium (M)	High (H)
Oil-type Viscosity (OV), in cSt	0 - 800 - 1300	1000 - 1500 - 2000	1600 - 3200 - 10000
Waves Height (WH), in m	0 - 0.15 - 0.4	0.3 - 0.73 - 1.0	0.75 - 1.2 - 3.0
Currents (CU), in knots	0 - 0.55 - 0.75	0.6 - 0.8 - 1.0	0.85 - 1.2 - 2.0
Water Depth (WD), in m	0 - 1.25 - 3.25	2.5 - 4.0 - 5.0	4.25 - 7.0 - 10.0

3.2.3 Oil recovery by using oil adsorbents/ sorbents

Oil adsorbents/ sorbents are materials that soak up liquids used for pollution prevention and oil recovery through the mechanisms of absorption, adsorption, or both. The main Linguistic Variables concerning oil recovery using oil absorbents – sorbents were formed by experts in oil spill fields, from researching on the literature survey (Dryud, 1989; Deschamps et al., 2003; Annunciado et al., 2005; Bayat et al., 2005) and studying the relevant ASTM Standard (F726, 2012). In Table 3.3 these Linguistic Variables for the case of oil recovery by using oil adsorbents/ sorbents as oil anti-pollution method are presented. Oil adsorbents/ sorbents are obliged to have the suitability approval by the MSMAA according to Ministerial Decision 1218.91/97 [Government Gazette 951 B/23-10-1997] in order to be used in the Greek territory.

Table 3.3 Linguistic variables for the case of oil recovery by using oil adsorbents/ sorbents

Linguistic variables	Categorization		
	Low (L)	Medium (M)	High (H)
Oil-type Viscosity (OV), in cSt	0 - 800 - 1300	1000 - 1500 - 2000	1600 - 3200 - 10000
Oil Thickness (OT), in mm	0 - 2.4 - 3.9	3.0 - 5.3 - 8.0	5.6 - 9.3 - 12.0
Wind Speed (WS), in knots	0 - 5 - 13	10 - 16 - 23	17 - 30 - 50

3.2.4 Oil containment by using oil booms

Booms or oil containment booms are floating devices which extend above and below the water surface and may have one or more of the following functions in connection with oil spill response on water: deflecting oil to prevent that the oil slick hits sensitive areas; containment and concentration of oil. The main Linguistic Variables concerning oil containment by using booms were formed by experts in oil spill fields, from researching on the literature survey (Goodman et al., 1996; Muttin, 2008; Yang and Liu, 2013) and studying the relevant ASTM Standards (D751, 2011; F625, 2000; F715, 2012; F818, 2003; F1093, 2012; F2084, 2001). Oil booms are obliged to have the suitability approval by the MSMAA according to Ministerial Decision 3221.2/1/99 [Government Gazette 76 B/08-02-1999] in order to be used in the Greek territory. In Table 3.4 these Linguistic Variables for the case of oil containment by using oil booms as oil anti-pollution method are presented.

Table 3.4 Linguistic variables for the case of oil containment by using oil booms

Linguistic variables	Categorization		
	Low (L)	Medium (M)	High (H)
Wind Speed (WS), in knots	0 - 5 - 13	10 - 16 - 23	17 - 30 - 50
Waves Height (WH), in m	0 - 0.15 - 0.4	0.3 - 0.73 - 1.0	0.75 - 1.2 - 3.0
Currents (CU), in knots	0 - 0.55 - 0.75	0.6 - 0.8 - 1.0	0.85 - 1.2 - 2.0
Type of Sea Area (TSA), empirical characterization	0 - 0.27 - 0.45 C: closed	0.35 - 0.56 - 0.7 SC: semi - closed	0.6 - 0.82 - 1.0 OS: open sea

3.2.5 Use of chemicals dispersants

Dispersants are a group of chemicals designed to be sprayed onto oil slicks, to accelerate the process of natural dispersion.

Table 3.5 Linguistic variables for the case of the use of chemicals dispersants

Linguistic variables	Categorization		
	Low (L)	Medium (M)	High (H)
Wind Speed (WS), in knots	0 - 5 - 13	10 - 16 - 23	17 - 30 - 50
Distance from populated, touristy or ecologically sensitive areas (DFA), in km	0 - 1.3 - 2.6	2.0 - 3.2 - 5.0	3.5 - 6.5 - 8.0
Salinity (SL), in $^{0}/_{oo}$ degrees salinity	0 - 31 - 42	40 - 45 - 50	47 - 58 - 60
Oil-type Viscosity (OV), in cSt	0 - 800-1300	1000-1500-2000	1600 - 3200 - 10000
Quantity of escaped Oil into the sea (QO), in tn	0 - 10 - 200	150 - 450 - 750	600 - 870 - 1000

The main Linguistic Variables concerning use of chemical dispersants as oil antipollution method were formed by experts in oil spill fields, from researching on the literature survey (Mackay, 1995; Fingas et al., 1995a; Fingas et al., 1995b; Daling et al., 2002; Otitoloju and Popoola, 2009; Fingas, 2011b) and studying the relevant ASTM Standard (F1737, 1999). In Table 3.5 these Linguistic Variables for the case of the use of chemicals dispersants as oil anti-pollution method are presented.

3.3 Methods of combating oil pollution via Rules Index

In the previous subsection oil pollution combating methods depending on their linguistic variables were introduced. In this subsection the above methods expressed via Rules Index will be presented in order to be connected to a wider context of marine oil pollution contingency planning. It should be mentioned that in “if part” OR has exclusive mean, while in “then part” OR has inclusive mean.

3.3.1 In–situ burning

In Table 3.6 the Rules Index for the case of the in-situ burning as anti oil pollution method are presented. In “then part”: In-Situ Burning is recommended (R), high recommended (HR) and no recommended (NR).

Table 3.6 Rules Index for the case of in-situ burning

If part	Then
DFA is L OR OT is L OR WS is H OR WH is H	ISB is NR
DFA is M AND OT is M AND WS is (L OR M) AND WH is (L OR M)	ISB is R
DFA is H AND OT is H AND WS is (L OR M) AND WH is (L OR M)	ISB is HR
DFA is M AND OT is H AND WS is L AND WH is (L OR M)	ISB is R
DFA is H AND OT is M AND WS is L AND WH is (L OR M)	ISB is R
DFA is M AND OT is H AND WS is M AND WH is L	ISB is HR
DFA is M AND OT is H AND WS is M AND WH is M	ISB is R
DFA is H AND OT is M AND WS is M AND WH is L	ISB is HR
DFA is H AND OT is M AND WS is M AND WH is M	ISB is R

3.3.2 Oil recovery by using oil skimmers

A short description of oil skimmers used in this study follows: Boom Skimmers (BOS) include any device in which the skimmer is incorporated in the face of the containment boom, regardless of the skimmer type. Brush Skimmers (BRS) are oleophilic skimmers that pick up oil on the bristles of a brush. Oleophilic Disc Skimmers (ODiS) use the principle of oil adhering to a solid surface, and typically include a series of discs that are rotated through the slick. As each disc is rotated through the oil/water interface, oil adheres to the disc surface and is then removed by scrapers mounted on both sides of each disc. Star Disc Skimmer (SDS) uses rotating discs to recover oil through mechanical, rather than oleophilic principles. Oleophilic Drum Skimmers (ODrS) uses adhesion of oil to the surface of a cylindrical drum for recovery. As the skimmer drum is rotated through the slick, oil adheres to the drum surface and is scraped off into a sump and then pumped away. Helical Drum Skimmers (HDS) employ the rotation of the drum to generate a current that draws oil into the drum. Paddle Belt Skimmers (PBS) use a series of paddles, attached to a belt, to lift oil out of the water. Stationary Rope Mop Skimmers (SRMS). In SRMS the rope loop is pulled through a wringer that removes oil along with some water.

Table 3.7 Skimmer's type and linguistic variables related to oil recovery

#	Skimmer's type	Viscosity	Wave Height	Currents	Water Depth
1	BOS	L - M	L - M	L – M	M – H
2	BRS	M - H	L - M	L – M – H	M – H
3	ODiS	L - M	L - M	L – M	L – M - H
4	SDS	H	L – M - H	L – M	L – M - H
5	ODrS	L – M - H	L - M	L – M	L – M - H
6	HDS	H	L - M	L	M – H
7	PBS	M - H	L - M	L	M – H
8	SRMS	L - M	L - M	L	L – M - H
9	SMS	L - M	L - M	L	L – M - H
10	ZRVS	L - M	L - M	L – M – H	M – H
11	SBS	M - H	L – M - H	L – M – H	M – H
12	FSPS	L - M	L – M - H	L – M – H	M – H
13	SMPS	L – M - H	L – M - H	L – M – H	M – H
14	SSS	L - M	L - M	L – M	L – M - H
15	AC	L – M - H	L - M	L – M	L – M - H
16	WSEP	L - M	L - M	L – M	L – M - H
17	WSIP	L - M	L - M	L – M	M – H
18	IFWS	L - M	L - M	L	M – H
19	AWeS	L – M - H	L - M	L – M – H	M – H

Suspended Mop Skimmers (SMS) use several mops that go through a skimmer head that is suspended over the skimming area with a crane. Zero Relative Velocity Skimmers (ZRVS) are rope mop devices used in catamaran hull vessels. A series of separate ropes (generally four to six) are arranged between the hulls. They are allowed to hang loosely on the water surface and are rotated aft at a velocity close to the forward speed of the vessel. Velocity of the ropes relative to the oil on the water is close to zero.

Sorbent Belt Skimmers (SBS) use an oleophilic belt to recover oil. The belt is made of porous oleophilic material that allows the water to pass through. The belt is positioned at an angle to the water with the leading edge of the belt immersed in the slick. At the top of its rotation the belt passes through a set of rollers where oil and water are removed from the belt through a combination of scraping and squeezing.

Fixed Submersion Plane Skimmers (FSPS) present a fixed or stationary plane to the oil/water interface as the skimmer is advanced through a slick. The plane causes an oil/water mixture to be submerged, and the buoyant force of the oil directs it up to a collection well.

Table 3.8 Rules Index for the case of the oil recovery by using oil skimmers

If part	Then
OV is (L OR M) AND WH is (L OR M) AND CU is L AND WD is L	USE ODiS OR ODrS OR SRMS OR SMS OR SSS OR AC OR WSEP
OV is L AND WH is (L OR M) AND CU is L AND WD is (M OR H)	USE BOS OR ODiS OR ODrS OR SRMS OR SMS OR ZRVS OR FSPS OR SMPS OR SSS OR AC OR WSEP OR WSIP OR IFWS OR AWeS
OV is (L OR M) AND WH is (L OR M) AND CU is M AND WD is L	USE ODiS OR ODrS OR SSS OR AC OR WSEP
OV is L AND WH is (L OR M) AND CU is M AND WD is (M OR H)	USE BOS OR ODiS OR ODrS OR ZRVS OR FSPS OR SMPS OR SSS OR AC OR WSEP OR WSIP OR IFWS OR AWeS
OV is (L OR M) AND WH is (L OR M) AND CU is H AND WD is L	DO NOT USE SKIMMERS
OV is L AND WH is (L OR M) AND CU is H AND WD is (M OR H)	USE ZRVS OR FSPS OR SMPS OR AWeS
OV is L AND WH is H AND CU is (L OR M OR H) AND WD is L	DO NOT USE SKIMMERS
OV is L AND WH is H AND CU is (L OR M OR H) AND WD is (M OR H)	USE FSPS OR SMPS
OV is M AND WH is (L OR M) AND CU is L AND WD is (M OR H)	USE BOS OR BRS OR ODiS OR ODrS OR PBS OR SRMS OR SMS OR ZRVS OR SBS OR FSPS OR SMPS OR SSS OR AC OR WSEP OR WSIP OR IFWS OR AWeS
OV is M AND WH is (L OR M) AND CU is M AND WD is (M OR H)	USE BOS OR BRS OR ODiS OR ODrS OR ZRVS OR SBS OR FSPS OR SMPS OR SSS OR AC OR WSEP OR WSIP OR AWeS
OV is M AND WH is (L OR M) AND CU is H AND WD is (M OR H)	USE BRS OR ZRVS OR SBS OR FSPS OR SMPS OR AWeS
OV is M AND WH is H AND CU is (L OR M OR H) AND WD is L	DO NOT USE SKIMMERS
OV is M AND WH is H AND CU is (L OR M OR H) AND WD is (M OR H)	USE SBS OR FSPS OR SMPS
OV is H AND WH is (L OR M) AND CU is (L OR M) AND WD is L	USE SDS OR ODrS OR AC
OV is H AND WH is (L OR M) AND CU is L AND WD is (M OR H)	USE BRS OR SDS OR ODrS OR HDS OR PBS OR SBS OR SMPS OR AC OR AWeS
OV is H AND WH is (L OR M) AND CU is M AND WD is (M OR H)	USE BRS OR SDS OR ODrS OR SBS OR SMPS OR AC OR AWeS
OV is H AND WH is (L OR M OR H) AND CU is H AND WD is L	DO NOT USE SKIMMERS
OV is H AND WH is (L OR M) AND CU is H AND WD is (M OR H)	USE BRS OR SBS OR SMPS OR AWeS
OV is H AND WH is H AND CU is (L OR M) AND WD is L	USE SDS
OV is H AND WH is H AND CU is (L OR M) AND WD is (M OR H)	USE SDS OR SBS OR SMPS
OV is H AND WH is H AND CU is H AND WD is (M OR H)	USE SBS OR SMPS

Submersion Moving Plane Skimmers (SMPS) present a moving plane, typically a conveyor-belt like material, to the oil/ water interface and directs it under water to a collection well. The collection well has discharge ports along its bottom, allowing water to be released and providing gravity oil/ water separation. Stationary Suction Skimmers (SSS) include any simple suction head used on a hose from a vacuum truck or a portable pump. To be considered in this category the skimming head must only be a suction device and not include any oil/water separation device such as a weir. Air Conveyors (AC) are also used as suction skimmers. In these systems oil and water are picked up at high velocity and carried through a large diameter hose into a large reception bin.

Weir Skimmers with External Pumps (WSEP) and Weir Skimmers with Integral Pumps (WSIP) include any weir device that uses gravity to drain oil off the water surface. Induced Flow Weir Skimmers (IFWS) use a mechanical or hydrodynamic force to draw oil to and over the weir. Advancing Weir Skimmers (AWeS) are a variation on conventional weirs in that the forward motion of the skimming system provides the flow into the skimmer. In Table 3.7, skimmer's type and linguistic variables related to oil recovery are presented. In Table 3.8 the Rules Index for the case of the oil recovery by using oil skimmers as anti oil pollution method are presented.

3.3.3 Oil recovery by using oil adsorbents/ sorbents

In Table 3.9 the Rules Index for the case of the oil recovery by using oil adsorbents/ sorbents as anti oil pollution method are presented. A division of oil adsorbents/ sorbents materials follows. Absorbent Materials (AMa) include: Absorbent Rolls (ARo), Absorbent Pads (APa) and Absorbent Pillows (APi). Sorbent Materials include: Sorbent Socks (SSo). In "then part": Use of AMa OR SSo is recommended (R), high recommended (HR) and no recommended (NR).

Table 3.9 Rules Index for the case of the oil recovery by using oil adsorbents/sorbents

If part	Then
OT is L	Use of AMa OR SSo is NR
WS is H	Use of AMa OR SSo is NR
OV is (L OR M) AND OT is (M OR H) AND WS is L	Use of AMa is HR
OV is (L OR M) AND OT is (M OR H) AND WS is M	Use of AMa is R
OV is H AND OT is (M OR H) AND WS is L	Use of SSo is HR
OV is H AND OT is (M OR H) AND WS is M	Use of SSo is R

3.3.4 Oil containment by using oil booms

In Table 3.10 the Rules Index for the case of the oil containment by using oil booms as anti oil pollution methods are presented. A division of oil booms follows: Open Water Boom (OWB) is a boom intended for use in open waters and Protected Water Boom (PWB) is a boom intended for use in protected waters. In “then part”: USE OF OWB is low recommended (LR), medium recommended (MR), high recommended (HR), USE OF PWB is low recommended (LR), medium recommended (MR), high recommended (HR) and there is the possibility of DO NOT USE BOOMS.

Table 3.10 Rules Index for the case of the oil containment by using oil booms

If part	Then
WS is L AND WH is (L OR M) AND CU is L AND TSA is (L OR M)	USE OF PWB is HR
WS is L AND WH is (L OR M) AND CU is L AND TSA is H	USE OF OWB is HR
WS is (L OR M) AND WH is (L OR M) AND CU is (M OR H) AND TSA is (L OR M)	USE OF PWB is LR
WS is (L OR M) AND WH is (L OR M) AND CU is (M OR H) AND TSA is H	USE OF OWB is LR
WS is (L OR M) AND WH is H AND CU is L AND TSA is (L OR M)	USE OF PWB is LR
WS is (L OR M) AND WH is H AND CU is L AND TSA is H	USE OF OWB is LR
WS is (L OR M) AND WH is H AND CU is (M OR H)	DO NOT USE BOOMS
WS is M AND WH is L AND CU is L AND TSA is (L OR M)	USE OF PWB is HR
WS is M AND WH is L AND CU is L AND TSA is H	USE OF OWB is HR
WS is M AND WH is M AND CU is L AND TSA is (L OR M)	USE OF PWB is MR
WS is M AND WH is M AND CU is L AND TSA is H	USE OF OWB is MR
WS is H AND WH is (L OR M) AND CU is L AND TSA is (L OR M)	USE OF PWB is LR
WS is H AND WH is (L OR M) AND CU is L AND TSA is H	USE OF OWB is LR
WS is H AND WH is (L OR M) AND CU is (M OR H)	DO NOT USE BOOMS
WS is H AND WH is H	DO NOT USE BOOMS

3.3.5 Use of chemicals dispersants

In Table 3.11 the Rules Index for the case of the use of chemicals dispersants as anti oil pollution method are presented. In “then part”: Vessel Dispersion (VD) is low recommended (LR), medium recommended (MR), high recommended (HR), Aerial Dispersion (AD) is low recommended (LR), medium recommended (MR), high recommended (HR) and there is the possibility of DO NOT USE CHEMICALS.

Table 3.11 Rules Index for the case of the use of chemicals dispersants

If part	Then
WS is (L OR M) AND DFA is (L OR M OR H) AND SL is (L OR M OR H) AND OV is H	DO NOT USE CHEMICALS
WS is M AND DFA is M AND SL is M AND OV is L AND QO is L	VD is HR
WS is M AND DFA is M AND SL is M AND OV is L AND QO is M	VD OR AD is HR
WS is M AND DFA is M AND SL is M AND OV is L AND QO is H	AD is HR
WS is M AND DFA is H AND SL is M AND OV is (L OR M) AND QO is L	VD is HR
WS is M AND DFA is H AND SL is M AND OV is (L OR M) AND QO is M	VD OR AD is HR
WS is M AND DFA is H AND SL is M AND OV is (L OR M) AND QO is H	AD is HR
WS is L AND DFA is H AND SL is M AND OV is L AND QO is L	VD is HR
WS is L AND DFA is H AND SL is M AND OV is L AND QO is M	VD OR AD is HR
WS is L AND DFA is H AND SL is M AND OV is L AND QO is H	AD is HR
WS is L AND DFA is L AND SL is (L OR H) AND OV is M AND QO is L	VD is LR
WS is L AND DFA is L AND SL is (L OR H) AND OV is M AND QO is M	VD OR AD is LR
WS is L AND DFA is L AND SL is (L OR H) AND OV is M AND QO is H	AD is LR
WS is L AND DFA is (L OR M) AND SL is (L OR M OR H) AND OV is L AND QO is L	VD is MR
WS is L AND DFA is (L OR M) AND SL is (L OR M OR H) AND OV is L AND QO is M	VD OR AD is MR
WS is L AND DFA is (L OR M) AND SL is (L OR M OR H) AND OV is L AND QO is H	AD is MR
WS is L AND DFA is M AND SL is (L OR M OR H) AND OV is M AND QO is L	VD is MR
WS is L AND DFA is M AND SL is (L OR M OR H) AND OV is M AND QO is M	VD OR AD is MR
WS is L AND DFA is M AND SL is (L OR M OR H) AND OV is M AND QO is H	AD is MR
WS is L AND DFA is L AND SL is M AND OV is M AND QO is L	VD is MR
WS is L AND DFA is L AND SL is M AND OV is M AND QO is M	VD OR AD is MR
WS is L AND DFA is L AND SL is M AND OV is M AND QO is H	AD is MR
WS is M AND DFA is L AND SL is (L OR M OR H) AND OV is (L OR M) AND QO is L	VD is MR
WS is M AND DFA is L AND SL is (L OR M OR H) AND OV is (L OR M) AND QO is M	VD OR AD is MR
WS is M AND DFA is L AND SL is (L OR M OR H) AND OV is (L OR M) AND QO is H	AD is MR
WS is M AND DFA is M AND SL is (L OR H) AND OV is (L OR M) AND QO is L	VD is MR
WS is M AND DFA is M AND SL is (L OR H) AND OV is (L OR M) AND QO is M	VD OR AD is MR
WS is M AND DFA is M AND SL is (L OR H) AND OV is (L OR M) AND QO is H	AD is MR
WS is M AND DFA is M AND SL is M AND OV is M AND QO is L	VD is MR
WS is M AND DFA is M AND SL is M AND OV is M AND QO is M	VD OR AD is MR
WS is M AND DFA is M AND SL is M AND OV is M AND QO is H	AD is MR
WS is (L OR M) AND DFA is H AND SL is (L OR H) AND OV is (L OR M) AND QO is L	VD is MR
WS is (L OR M) AND DFA is H AND SL is (L OR H) AND OV is (L OR M) AND QO is M	VD OR AD is MR
WS is (L OR M) AND DFA is H AND SL is (L OR H) AND OV is (L OR M) AND QO is H	AD is MR
WS is L AND DFA is H AND SL is M AND OV is M AND QO is L	VD is MR
WS is L AND DFA is H AND SL is M AND OV is M AND QO is M	VD OR AD is MR
WS is L AND DFA is H AND SL is M AND OV is M AND QO is H	AD is MR
WS is H	DO NOT USE CHEMICALS

3.4 Combination of methods of combating oil pollution via Rules Index

Methods of combating oil pollution include: in-situ burning, oil recovery, oil containment/ recovery and use of chemical dispersants. In subsection 3.3, Rules Index was presented to show the influence of crucial linguistic variables in the use of each method. Contingency plan, as it is described in subsection 3.1, includes the methods mentioned above; operates in a dynamic basis and formed in a chronically sequence mode. In this subsection Rules Index that deal with the selection of the suitable way to combat oil pollution are formed while an oil spill anti-pollution method has already been used. It should be mentioned that in “if part” OR has exclusive mean, while in “then part” OR has inclusive mean.

3.4.1 Oil recovery while chemical dispersants have already been used

At this point, Rules Index that deals with the selection of the suitable mean to achieve oil recovery is created while chemical dispersants have already been used. Natural dispersion of an oil slick occurs when waves and other turbulence at the sea surface cause all or part of the slick to break up into droplets and enter into the water column. The addition of chemical dispersants is intended to accelerate this process. When a dispersant is sprayed onto an oil slick, the interfacial tension between the oil and water is reduced promoting the formation of finely dispersed oil droplets. If dispersion is successful, a characteristic plume will spread slowly down from the water surface a few minutes after treatment.

Unsuccessful use of chemical dispersants (UCD) may lead to oil recovery via sorbents. The procedure of trying to use chemical dispersants needs time and raises the viscosity of the spilled oil. At the same time with emulsification, raises the oil thickness. In Table 3.12 the Rules Index for the case of oil recovery by using oil adsorbents/ sorbents, after unsuccessful use of chemicals dispersants, as anti oil pollution method are presented.

Table 3.12 Rules Index for the case of oil recovery by using oil adsorbents/ sorbents, after unsuccessful use of chemicals dispersants

If part	Then
UCD AND OV is H AND OT is (M OR H) AND WS is L	Use of SSo is HR
UCD AND OV is H AND OT is (M OR H) AND WS is M	Use of SSo is R
UCD AND OV is H AND (OT is L OR WS is H)	Use of SSo is NR

3.4.2 Oil recovery while oil containment has already been achieved

Furthermore, Rules Index that connected with the choice of proper equipment to recover oil is designed while containment and concentration of oil has already been successfully done by using booms. Concentrated oil has grater thickness from the initial spilled oil and as required enough time-period to concentrate the oil by using booms, raises the viscosity of the spilled oil. So, successful use of booms (UB) in order to contain the spilled oil is followed by oil recovery using skimmers.

In Table 3.13 the Rules Index for the case of oil recovery by using oil skimmers, after successful oil containment, as anti oil pollution method are presented.

Table 3.13 Rules Index for the case of oil recovery by using oil skimmers, after successful oil containment

If part	Then
UB AND OV is H AND WH is L OR M AND CU is L OR M AND WD is L	USE SDS OR AC
UB AND OV is H AND WH is L OR M AND CU is L AND WD is M OR H	USE BRS OR SDS OR PBS OR SBS OR AC
UB AND OV is H AND WH is L OR M AND CU is M AND WD is M OR H	USE BRS OR SDS OR SBS OR AC
UB AND OV is H AND WH is L OR M AND CU is H AND WD is M OR H	USE BRS OR SBS
UB AND OV is H AND WH is H AND CU is L AND WD is L	USE SDS
UB AND OV is H AND WH is H AND CU is L AND WD is M OR H	USE SDS OR SBS

Peripheral tools of the Proposed National Contingency Plan

A simulation oil dispersion model, like the “GNOME” (developed by the Emergency Response Division of the National Oceanic and Atmospheric Administration of the U.S Department of Commerce, could be used as a peripheral tool of the PNCP, in order to indicate the movement of an hypothetical oil spill towards time. GNOME (General NOAA Operational Modelling Environment) is the modelling tool the Emergency Response Division uses to predict the possible route, or trajectory, a pollutant might follow in or on a body of water, such as in an oil spill.

However, GNOME model helps to combat an oil spill by: (i) predicting how wind, currents, and other processes might move and spread oil spilled on the water; (ii) learning how these predictions of where and how oil might move are affected by uncertainty in observations and forecasts for ocean currents and wind; and (iii) seeing how spilled oil is expected to change chemically and physically, known as weathering, during the time that it remains on the water surface. Initially a spill scenario should be described by entering information into the program and then GNOME model creates and displays an oil spill "movie" showing the predicted trajectory of the oil spilled in the scenario (Fig. 3.2). In addition to this animation, GNOME estimates the amount of oil beached, still floating, or evaporated at specific times.

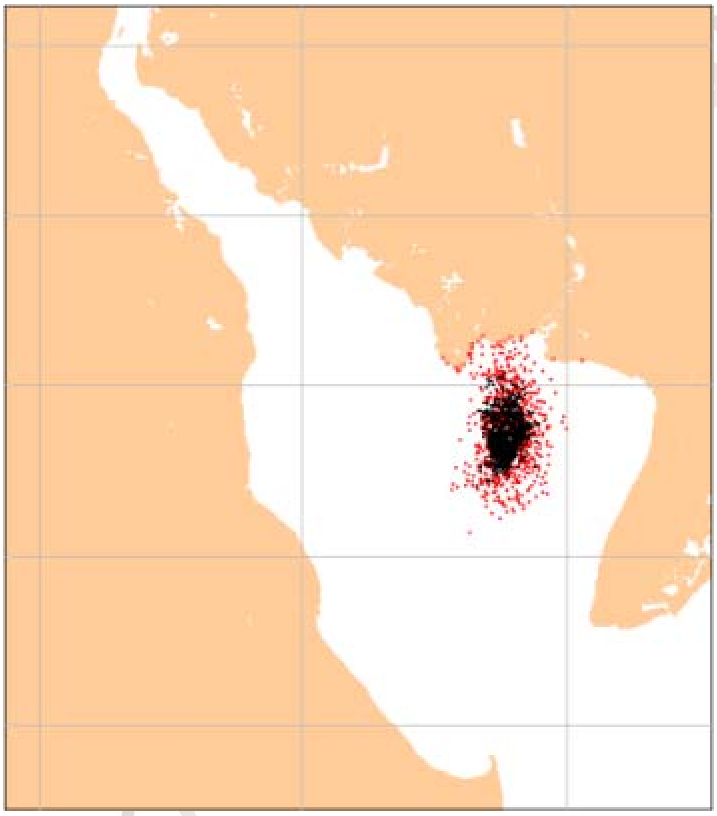


Fig. 3.2 GNOME model output depicting relative distribution of oil

A meteorological diagnostic model could be used as a peripheral tool of the PNCP, necessary for the impression and evolution of the wind field in the area of oil spill episode; "Poseidon" developed by the Hellenic Centre for Marine Research (Hellenic Centre for Marine Research, www.hcmr.gr/). This model uses wind speed and direction measured at meteorological stations in the area of interest, provided on-line (Poseidon model, www.poseidon.gr/), to compute wind speed and direction in every grid of the area through various previously tested gridding techniques and provides a meteorological chart showing wind speed and direction in every grid cell of the area of interest. The wind factor being variable, thus influencing both: the sea surface and the oil-slick movement, this procedure is repeated at regular time intervals (e.g., per hour). The network of observation buoys records continuously the physical, biological and chemical parameters of the Greek seas. The observation buoys are equipped with sensors that monitor: air-pressure, air temperature, wind speed and direction, wave height (period and direction), sea surface salinity and temperature, surface current speed and direction, sea surface dissolved oxygen, light attenuation with fluorescence, salinity and temperatures in depths 0-50 m, chlorophyll-a, nutrients and radioactivity. “Poseidon” supports a pollutants transport model, which aims to the forecast of the transport (3D advection, diffusion and bio-chemical transformations) and other relevant by-processes (such as sedimentation, beaching) of the buoyant pollutants introduced accidentally into the sea. The model receives information from the wave and ocean hydrodynamic prediction models and produces quantitative information (in the form of equal concentration distribution curves, or in other relevant forms, like streak lines etc) of the investigated pollutant. This model will be specifically adapted to the tracking of the spatio-temporal evolution of oil slicks and floating bodies.

CHAPTER 4
EVALUATION OF PNCP COMPARED TO GNCP

4.1 The case study of “Sitarem–Spirit” incident

4.1.1 Initial data

On March 12 1996 at about 22:50΄, in the position latitude 36^{o} 24.5΄N, longitude 22^{o} 57.8΄E at a distance of 1.2 n.m. (nautical miles) from Cape Spathi in Kythira Island (Fig. 4.1), cargo vessel “Sitarem” loaded with soil bound for Spain collided with tanker “Spirit” loaded with 67,000 tn of crude oil viscosity (OV) about 300 cSt, bound for Costanza, Romania. The weather at the area was calm with southeast winds of 4-5 BF. Wind speed (WS) was 16 knots, wave’s height (WH) was about 0.75 m and no significant sea currents were mentioned. Currents (CU) were about 0.30 knots. The type of sea area (TSA), characterized open - semi closed, was 0.6. Water salinity (SL) was low, about $39^{o/oo}$ degrees salinity. The area is qualified as sensitive marine ecosystem and local economy is exclusively based on tourism and fishing activities. It is also a heavy traffic area as there are a great number of ships bound for Western Mediterranean area and Gibraltar passing through it and several marine accidents have occurred in the area.

Collision of the two vessels, as resulted from the preliminary inquiry, was caused by heavy negligence of the Captains of both ships and non-compliance with International Collision Prevention Code (ICPC), (MSMAA, Decision no. 4/97). None of the two Captains reported the incident to the Authorities. The cargo vessel “Sitarem” was located on March 13 1996 at about 09:30΄, i.e., eleven hours after the collision, by HCG Officers of the Neapolis Vion Port Authority. It had run aground in Maggano site of Vatika area in the Gulf of Laconia in a distance from populated – touristy or ecologically sensitive areas (DFA) about 1.5 km and in a water depth (WD) about 25 m. The quantity of the spilled oil (QO) estimated to be 600 tn and the oil thickness (OT) about 2.35 mm. On March 14 1996, weather conditions worsened wind speed (WS) was 24 knots and wave’s height (WH) was about 1.1 m.

4.1.2 Actions taken

The Neapolis Vion Port Authority through information by the Air Force on March 13 1996 at about 10:40΄ notified MRCC. A HCG aircraft was immediately ordered to proceed on the spot for local inspection. At 14:30΄ HCG aircraft located the tanker about 18 n.m. east of the Cape Maleas in a standstill and oil spills around the vessel. It also noticed an oil spill covering 500 x 500 m^2 surface on the south near the vessel as well as an oil spill of 6.5 n.m. length and 50-150 m width north of the vessel; it was also reported that the vessel did not seem to cause any further pollution.

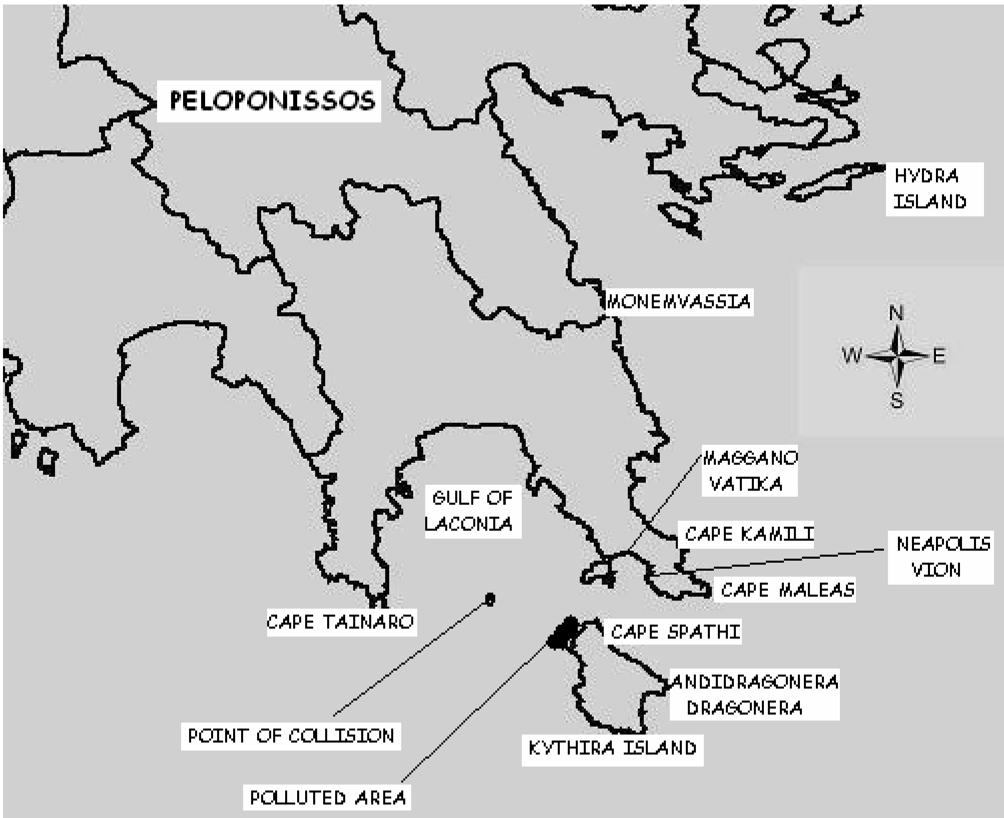


Fig. 4.1 The area of the “Sitarem” – “Spirit” incidence

Neapolis Vion Port Authority was ordered to use immediately an appropriate boat and to proceed on the spot for local evaluation of the situation and assessment of possible taking of anti-pollution action. HCG Patrol Boat 413 sailed from Central Piraeus Port Authority at 16:30′ bound for the sea area where the tanker was anchored in order to take antipollution action by using chemical dispersants on a limited scale. Furthermore, a private owned appropriate boat in the area of Neapolis Vion was standing by ready to take action provided with Port Authority appropriate antipollution material. The main Storehouse of the MEPD was standing by to provide washing substances, if required. It was evaluated that there was not any risk of coast pollution due to the big distance of the tanker and the oil spill from it. The ships’ owner companies were notified to take appropriate action. The Ministry of Foreign Affairs as well as the Embassies of the ships’ flag states was notified.

At night time, as the weather conditions worsened, the HCG Patrol Boat 413 remained anchored in Hydra Island. Unfavorable weather conditions did not permit a HCG aircraft or a boat on March 14 1996 to proceed to the area for a new inspection. In the area where the vessels collided north-northeast winds of 8-9 BF prevailed and visibility was poor. HCG Patrol Boat 413 remained in Hydra Island. Inspection of large shore areas in the vicinity of the collision area did not report any oil pollution.

HCG Patrol Boat 413 on March 17 1996 at about 07:10΄ sailed from Monemvassia port to inspect the coastline and the sea area in vicinity. At about 07.40΄ in a distance of 5 n.m. from the coast, between Cape Kamili and Cape Maleas the HCG Patrol Boat 413 located two strips of bubbles of about 200 m in length and 10 m width coming possibly of oil spill dispersion. At the Cape Maleas in a distance of 0.5 n.m. from the coast another strip of bubbles was located of about 1 n.m. length and 10 m width. The coastline was inspected but nothing was found; in the area were prevailed western winds of 4 BF. Upon order of the MRCC, HCG Patrol Boat 413 proceeded to Antidragonera and Dragonera skerries, east of Kythira Island to detect pollution reported by a HCG aircraft. At 14:40΄ HCG Patrol Boat 413 following inspection of the area located three strips, of about 100 m length and of 1 m width the biggest, of dispersed brown molecules, which did not require any antipollution action. The coastline was inspected to the extent possible, as water was shallow and nothing was found; at about 15:05΄ HCG Patrol Boat 413 was ordered by the MRCC to return to base. Neapolis Vion Port Authority on March 19 1996 imposed a fine on each vessel of 7,340 Euro for contravention to ICPC (Ministry of Mercantile Marine, Decision no. 4/97). The next day, a HCG aircraft and the Port Authority both reported that the spill’s rests were washed out on the coast of Diakofti Kythira and caused heavy oil pollution in a length of 1,000-1,500 m. It was also reported that the rest part of the spill had self-dispersed in the larger area of Cape Maleas and Kythira Island causing pollution problem.

4.2 Implementation of GNCP in “SITAREM–SPIRIT” incident

Pollution incidence was very severe, despite the fact that the main part of the spill was dispersed without any anti-pollution measures; its residues washed out in Diakofti Kythira and required long and hard effort (1 month’s work) by the HCG personnel, the Neapolis Vion Port Authority, local Authorities groups, and a private team sent by the representatives of tanker. Absorbing or insorbing material was used as well as manual means of collecting oil-polluted waste; rocks were washed with hot water under pressure. Subsequent analysis of the events indicated mainly significant delays in decision-making and action taken, as well as lack of exploitation of available resources. More specific:

- Local Port Authority reported the pollution incident eleven hours after the vessels' collision. Neapolis Vion Port Authority notified MRCC 70 min later, following information received by the Air Force, happening to fly over the area.
- Lack of surveillance and coordination of the Services involved is thus indicated.
- The incident was not reported by the two Captains and, since pollution could not be located by alternative means, as satellite remote sensing, there was a big delay which reduced the possibility of immediate/adequate response to the incident and increased considerably the pollution impact.
- There were no marine pollution incident scenarios of "what if…if then" type, as well as no strategies or alternatives to be followed. This is indicated by the fact that the RPCC at Neapolis Vion was not immediately activated (being the nearest competent Center) and, consequently, chemical dispersants have not been employed although local conditions (weather conditions, hydrodynamics prevailing in the specific area) were favourable at the time of the incidence and five days later.
- In addition, no other anti-pollution method has been ever considered (burn, oil recovery-containment, use of oil booms etc.).
- There was a significant misevaluation of oil spill dispersion on the basis of local weather conditions, owing to the scheduled reports that MRCC receives from the National Weather Service (every six hours) not permitting the prompt simulation of pollution dispersion, possible only if access to real time climate, oceanographic, hydrographical and weather data bases (winds force-direction, height of waves etc.) is feasible.
- Unfavourable weather conditions prevented the incidence survey by air for three days, as satellite surveillance is not available.

- No protection measures for the coastline of Diakofti Kythira have been taken, as pollution dispersion could not be predicted; as a result, heavy crude oil was spilled along 1,000-1,500 m of the coastline.

4.3 Implementation of PNCP in “SITAREM–SPIRIT” incident

Giving to our software system tool, all the necessary real conditions (10) linguistic variables, PNCP proposes antipollution solutions, directly oil recovery by using oil skimmers, oil containment by using oil booms, use of chemicals dispersants and after two days oil recovery by using oil skimmers (Table 4.1).

Table 4.1 Implementation of PNCP; directly and after two days

PNCP IMPLEMENTATION: DIRECT					
ISB					
DFA	OT	WS	WH		ISB
1.5	2.35	16	0.75		NR (0.8462)
OIL RECOVERY (by using oil adsorbents/ sorbents)					
OV	OT	WS			OIL RECOVERY (by using oil adsorbents/ sorbents
300	2.35	16			AMa OR SSo is NR (1.0000)
OIL RECOVERY (by using oil skimmers)					
OV	WH	CU	WD		OIL RECOVERY (by using oil skimmers)
300	0.75	0.3	25		Use 1,3,5,8,9,10,12,13,14,15,16,17,18,19 (from Table 3.7) (0.9259)
OIL CONTAINMENT (by using oil booms)					
WS	WH	CU	TSA		OIL CONTAINMENT (by using oil booms)
16	0.75	0.3	0.6		PWB is MR, OWB is NR (0.7143)
USE OF CHEMICALS DISPERSANTS					
WS	DFA	SL	OV	QO	USE OF CHEMICALS DISPERSANTS
16	1.5	39	300	600	VD OR AD is MR (0.2727)
PNCP IMPLEMENTATION: 2 DAYS LATER					
ISB					
DFA	OT	WS	WH		ISB
1.5	2.35	24	1.1		NR (0.5385)
OIL RECOVERY (by using oil adsorbents/ sorbents)					
OV	OT	WS			OIL RECOVERY (by using oil adsorbents/ sorbents)
300	2.35	24			AMa OR SSo is NR (0.5385)
OIL RECOVERY (by using oil skimmers)					
OV	WH	CU	WD		OIL RECOVERY (by using oil skimmers)
300	1.1	0.3	25		Use 12,13 (from Table 3.7) (0.7778)
OIL CONTAINMENT (by using oil booms)					
WS	WH	CU	TSA		OIL CONTAINMENT (by using oil booms)
24	1.1	0.3	0.6		PWB is NR, OWB is NR (0.5385)
USE OF CHEMICALS DISPERSANTS					
WS	DFA	SL	OV	QO	USE OF CHEMICALS DISPERSANTS
24	1.5	39	300	600	VD OR AD is NR (0.2727)

4.4 Discussion

The PNCP apart from the actions proposed to the previous sub-chapter considers as possible combined antipollution solutions, oil recovery by using oil skimmers after successful oil containment by using oil booms (directly and after two days) and directly oil recovery by using oil adsorbents/ sorbents after unsuccessful use of chemicals dispersants, (Tables 4.2, 4.3, respectively).

Table 4.2 Implementation of PNCP after successful oil containment by using oil booms; directly and after two days

PNCP IMPLEMENTATION: DIRECT				
OIL RECOVERY (by using oil skimmers)				
OV	WH	CU	WD	OIL RECOVERY (by using oil skimmers)
2000	0.75	0.3	25	Use 2,4,7,11,15 (from Table 3.7) (0.2500)
PNCP IMPLEMENTATION: 2 DAYS LATER				
OIL RECOVERY (by using oil skimmers)				
OV	WH	CU	WD	OIL RECOVERY (by using oil skimmers)
2000	1.1	0.3	25	Use 4,11 (from Table 3.7) (0.2500)

Table 4.3 Implementation of PNCP after unsuccessful use of chemicals dispersants; directly and after two days

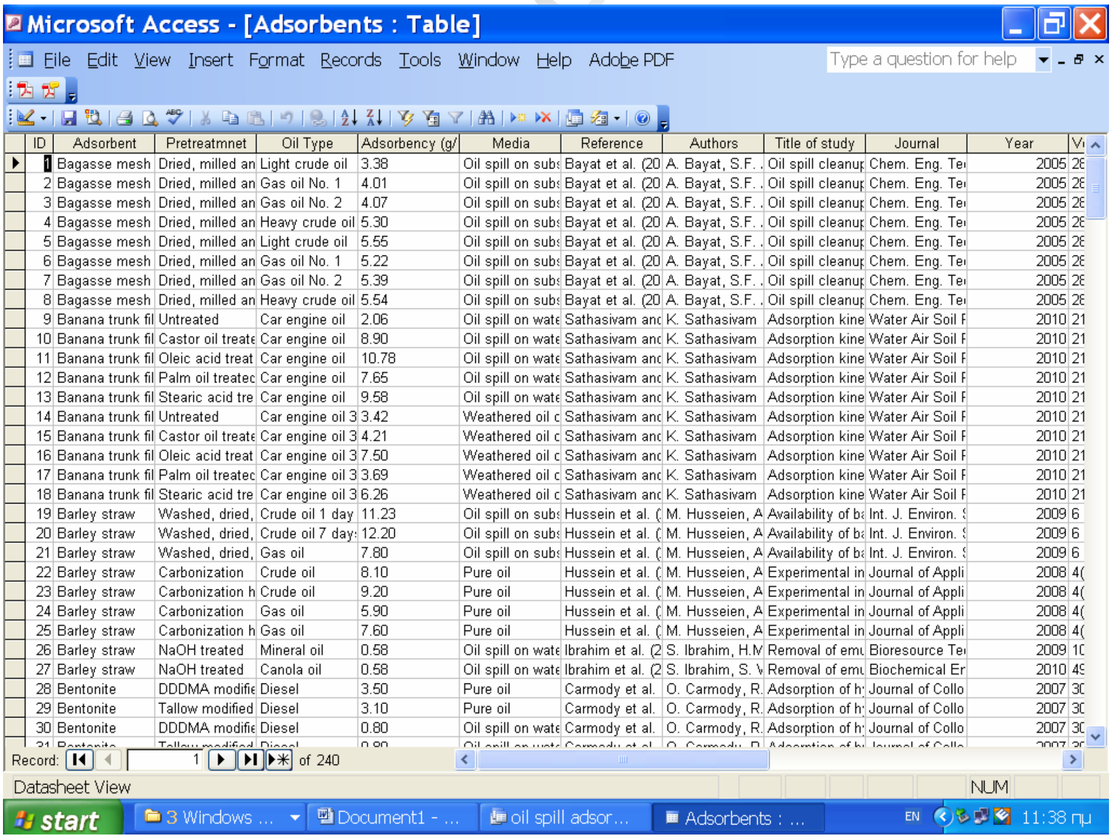
PNCP IMPLEMENTATION: DIRECT			
OIL RECOVERY (by using oil adsorbents/ sorbents)			
OV	OT	WS	OIL RECOVERY (by using oil adsorbents/ sorbents)
2000	4	16	SSo is R (0.2500)
PNCP IMPLEMENTATION: 2 DAYS LATER			
OIL RECOVERY (by using oil adsorbents/ sorbents			
OV	OT	WS	OIL RECOVERY (by using oil adsorbents/ sorbents)
2000	4	24	SSo is NR (0.2500)

CHAPTER 5
ADSORBENTS

5.1 Introduction

As mentioned in the subchapter 1.5, one of the decontamination methods for combating marine oil pollution is the use of adsorption media. Physical adsorption is defined as a reversible phenomenon in which molecules and atoms of a liquid or gas phase are retained on the surfaces of solid adsorbents with a large porous media. The reverse process is called desorption. The surface that holds substances called absorbent, while the restrained adsorbed substance called absorbate. The adsorption process is not used intensively for the treatment of wastewaters. Otherwise, the need to improve the quality of wastewaters and to reduce their toxicity has led to implementation of the adsorption process.

The phenomenon of adsorption is often confused with that of absorption, so it would be appropriate to clarify the difference between the two phenomena.

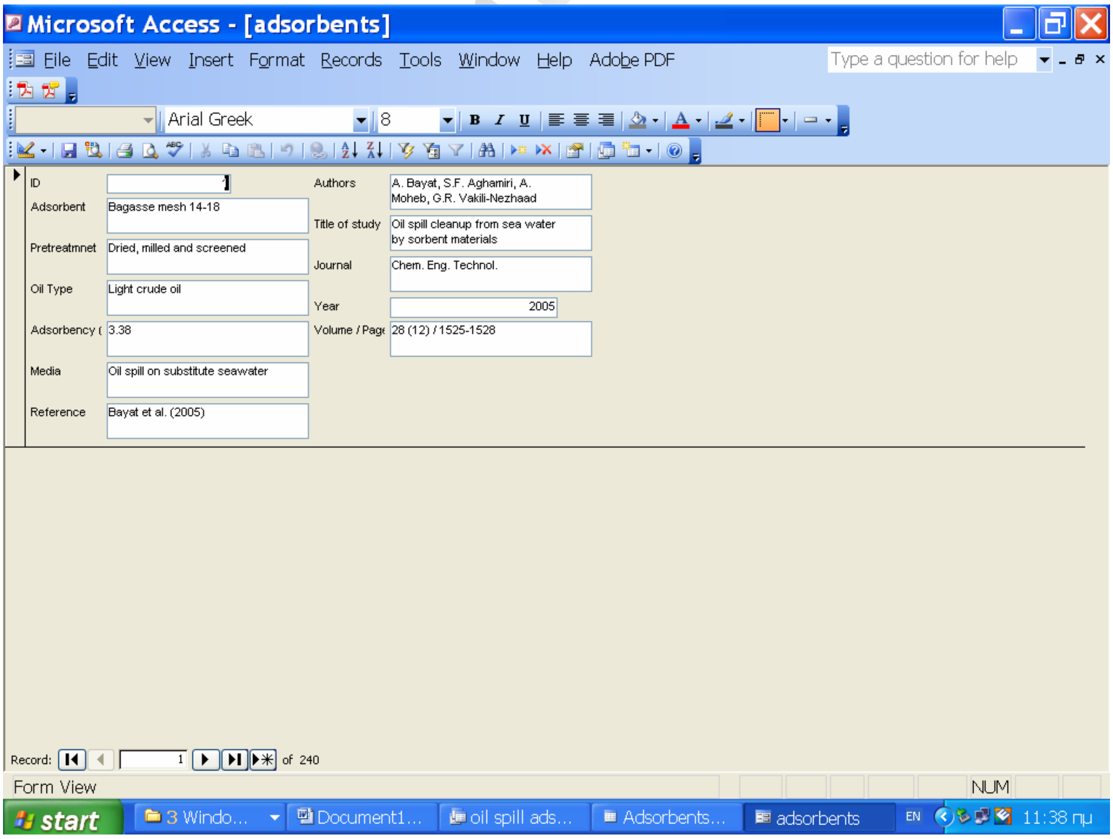


ID	Adsorbent	Pretreatmnet	Oil Type	Adsorbency (g/	Media	Reference	Authors	Title of study	Journal	Year	Vi
1	Bagasse mesh	Dried, milled an	Light crude oil	3.38	Oil spill on subs	Bayat et al. (20	A. Bayat, S.F. .	Oil spill cleanup	Chem. Eng. Tec	2005	28
2	Bagasse mesh	Dried, milled an	Gas oil No. 1	4.01	Oil spill on subs	Bayat et al. (20	A. Bayat, S.F. .	Oil spill cleanup	Chem. Eng. Tec	2005	28
3	Bagasse mesh	Dried, milled an	Gas oil No. 2	4.07	Oil spill on subs	Bayat et al. (20	A. Bayat, S.F. .	Oil spill cleanup	Chem. Eng. Tec	2005	28
4	Bagasse mesh	Dried, milled an	Heavy crude oil	5.30	Oil spill on subs	Bayat et al. (20	A. Bayat, S.F. .	Oil spill cleanup	Chem. Eng. Tec	2005	28
5	Bagasse mesh	Dried, milled an	Light crude oil	5.55	Oil spill on subs	Bayat et al. (20	A. Bayat, S.F. .	Oil spill cleanup	Chem. Eng. Tec	2005	28
6	Bagasse mesh	Dried, milled an	Gas oil No. 1	5.22	Oil spill on subs	Bayat et al. (20	A. Bayat, S.F. .	Oil spill cleanup	Chem. Eng. Tec	2005	28
7	Bagasse mesh	Dried, milled an	Gas oil No. 2	5.39	Oil spill on subs	Bayat et al. (20	A. Bayat, S.F. .	Oil spill cleanup	Chem. Eng. Tec	2005	28
8	Bagasse mesh	Dried, milled an	Heavy crude oil	5.54	Oil spill on subs	Bayat et al. (20	A. Bayat, S.F. .	Oil spill cleanup	Chem. Eng. Tec	2005	28
9	Banana trunk fil	Untreated	Car engine oil	2.06	Oil spill on wate	Sathasivam anc	K. Sathasivam	Adsorption kine	Water Air Soil F	2010	21
10	Banana trunk fil	Castor oil treate	Car engine oil	8.90	Oil spill on wate	Sathasivam anc	K. Sathasivam	Adsorption kine	Water Air Soil F	2010	21
11	Banana trunk fil	Oleic acid treat	Car engine oil	10.78	Oil spill on wate	Sathasivam anc	K. Sathasivam	Adsorption kine	Water Air Soil F	2010	21
12	Banana trunk fil	Palm oil treatec	Car engine oil	7.65	Oil spill on wate	Sathasivam anc	K. Sathasivam	Adsorption kine	Water Air Soil F	2010	21
13	Banana trunk fil	Stearic acid tre	Car engine oil	9.58	Oil spill on wate	Sathasivam anc	K. Sathasivam	Adsorption kine	Water Air Soil F	2010	21
14	Banana trunk fil	Untreated	Car engine oil 3	3.42	Weathered oil c	Sathasivam anc	K. Sathasivam	Adsorption kine	Water Air Soil F	2010	21
15	Banana trunk fil	Castor oil treate	Car engine oil 3	4.21	Weathered oil c	Sathasivam anc	K. Sathasivam	Adsorption kine	Water Air Soil F	2010	21
16	Banana trunk fil	Oleic acid treat	Car engine oil 3	7.50	Weathered oil c	Sathasivam anc	K. Sathasivam	Adsorption kine	Water Air Soil F	2010	21
17	Banana trunk fil	Palm oil treatec	Car engine oil 3	3.69	Weathered oil c	Sathasivam anc	K. Sathasivam	Adsorption kine	Water Air Soil F	2010	21
18	Banana trunk fil	Stearic acid tre	Car engine oil 3	6.26	Weathered oil c	Sathasivam anc	K. Sathasivam	Adsorption kine	Water Air Soil F	2010	21
19	Barley straw	Washed, dried,	Crude oil 1 day	11.23	Oil spill on subs	Hussein et al. (	M. Husseien, A	Availability of ba	Int. J. Environ. S	2009	6
20	Barley straw	Washed, dried,	Crude oil 7 days	12.20	Oil spill on subs	Hussein et al. (	M. Husseien, A	Availability of ba	Int. J. Environ. S	2009	6
21	Barley straw	Washed, dried,	Gas oil	7.80	Oil spill on subs	Hussein et al. (	M. Husseien, A	Availability of ba	Int. J. Environ. S	2009	6
22	Barley straw	Carbonization	Crude oil	8.10	Pure oil	Hussein et al. (	M. Husseien, A	Experimental in	Journal of Appli	2008	4(
23	Barley straw	Carbonization h	Crude oil	9.20	Pure oil	Hussein et al. (	M. Husseien, A	Experimental in	Journal of Appli	2008	4(
24	Barley straw	Carbonization	Gas oil	5.90	Pure oil	Hussein et al. (	M. Husseien, A	Experimental in	Journal of Appli	2008	4(
25	Barley straw	Carbonization h	Gas oil	7.60	Pure oil	Hussein et al. (	M. Husseien, A	Experimental in	Journal of Appli	2008	4(
26	Barley straw	NaOH treated	Mineral oil	0.58	Oil spill on wate	Ibrahim et al. (2	S. Ibrahim, H.M	Removal of emu	Bioresource Tec	2009	1(
27	Barley straw	NaOH treated	Canola oil	0.58	Oil spill on wate	Ibrahim et al. (2	S. Ibrahim, S. V	Removal of emu	Biochemical En	2010	4(
28	Bentonite	DDDMA modifie	Diesel	3.50	Pure oil	Carmody et al.	O. Carmody, R.	Adsorption of hy	Journal of Collo	2007	30
29	Bentonite	Tallow modified	Diesel	3.10	Pure oil	Carmody et al.	O. Carmody, R.	Adsorption of hy	Journal of Collo	2007	30
30	Bentonite	DDDMA modifie	Diesel	0.80	Oil spill on wate	Carmody et al.	O. Carmody, R.	Adsorption of hy	Journal of Collo	2007	30

Fig. 5.1 Knowledge base in Microsoft Access form

Absorption is called the phenomenon in which the particles of foreign matter enter (penetrate) between absorbent particles. The adsorption is instead a superficial phenomenon, since the adsorbed substance accumulates on the surface of the adsorbent medium. In fact, the phenomenon of adsorption does not occur alone, but always accompanied with the phenomenon of absorption at low levels.

Initially the phenomenon of adsorption was observed on the surfaces of solids, which are sources of traction forces, because their atoms bordering sided with like atoms of the solid lattice. In this way, the free units, created in the affinity of the solid surface, can hold foreign atoms or molecules very strongly. Later the phenomenon of adsorption was observed in wet surfaces, which retain contaminants weaker than the solids. Many solids are used as sorbents to remove various impurities from liquids. The common sorbents have typically high surface area per unit mass, while the best known of these is silicon (silica gel), the active aluminum (activated alumina) and activated carbon. Activated charcoal is widely used as adsorbent in the process of water purification. Sorbents can be: inorganic mineral products, organic synthetic products or organic natural products.



ID: 1
Adsorbent: Bagasse mesh 14-18
Pretreatmnet: Dried, milled and screened
Oil Type: Light crude oil
Adsorbency (: 3.38
Media: Oil spill on substitute seawater
Reference: Bayat et al. (2005)
Authors: A. Bayat, S.F. Aghamiri, A. Moheb, G.R. Vakili-Nezhaad
Title of study: Oil spill cleanup from sea water by sorbent materials
Journal: Chem. Eng. Technol.
Year: 2005
Volume / Page: 28 (12) / 1525-1528

Fig. 5.2 A snapshot of the knowledge base

The last subcategory contains, inter alia, waste biomass coming from lignocellulosic residues left in farms or useless byproducts of agro-industrial units. The modification of such materials (usually hydrolysis with salts) can provide sorbents that have improved qualities for the adsorption of dyes and heavy metals (Batzias et al., 2009; Batzias and Sidiras, 2007a; Batzias and Sidiras 2007b; Batzias and Sidiras 2007c; Mohan and Pittman, 2006; Srinivasan and Viraraghavan, 2008).

A knowledge base in Microsoft Access form (Figs 5.1 and 5.2) was created for the needs of the Thesis. This knowledge base includes data about the adsorbents that were used, the kind of pretreatment, the oil type, the adsorbency, the media in which this adsorbency was measured, the authors names, the title of the study, the name of the referred journal and the year of publication.

5.2 Use of lignocellulosic materials as oil adsorbents

Literature survey shows that researchers used numerous untreated and pretreated lignocellulosic materials as adsorbents for oil spill cleaning. Some of the untreated materials are: barley straw (Witka-Jezewska et al., 2003; Husseien et al., 2009), bagasse (Said et al., 2009), cotton grass fiber (Suni et al., 2004), cotton grass mats (Suni et al., 2004), rice husk (Khan et al., 2004), garlic/onions peels (Sayed and Zayed, 2006), groundnut husks (Nwokoma and Avene, 2010), peat (Suni et al., 2004; Viraraghavan and Mathavan, 1988), and walnut shell (Srinivasan and Viraraghavan, 2008). Some of the pretreated materials are: acetylated wheat straw (Sun et al., 2004b), acetylated rice straw (Sun et al., 2002), acetylated sugarcane bagasse (Sun et al., 2004a), carbonized fir fibers (Inagaki et al., 2002), carbonized pith bagasse (Hussein, et al., 2008), carbonized rice husk (Kumagai et al., 2007; Angelova et al., 2011), fatty acid grafted sawdust (Banerjee et al., 2006a), pretreated banana trunk fiber (Sathasivam and Harris, 2010), heated barley straw (Husseien et al., 2008) and NaOH-treated barley straw (Ibrahim et al., 2009 and 2010).

5.2.1 Untreated lignocellulosic materials

Husseien et al. (2009) examined the absorption capacity of raw barley straw for different petroleum products and water pick up. Their investigation revealed that the capacity of fibers to remove crude oil from sea water was related to the surface properties of the fibers, concentration of the oil, size of the fiber, amount of the fibers, as well as the temperature of the crude oil. They demonstrated cyclic sorption/ desorption studies which indicated that a simple squeezing operation was enough to remove most of the sorbed oil so recycling was feasible. The oil sorption capacity was found to be dependent on the sorption time and on the system condition such as oil temperature and film thickness. The sorbed oil was removed from sorbent by a simple mechanical press suggesting the reusing of the sorbent for several times. Also, they found that the amount of water pick up was small due to wax layer covering the barley straw tissue. Finally, they proved that their sorbent can be reused 3 times to reach 50% of the first sorption value. Their results suggested that substitution of commercial synthetic oil sorbents in oil spill cleanup is possible by agriculture residue and could be beneficial by incorporating other advantages such as biodegradability.

Bayat et al. (2005) compared the performances of three different sorbents, bagasse, rice hull and polypropylene nonwoven web, in terms of oil sorption capacity and oil recovery efficiency. The sorbents were selected from natural (bagasse and rice hull) and synthetic (polypropylene nonwoven web) categories. Their experiments have been conducted to cleanup four different oil samples (light crude oil, gas oil No.1, gas oil No.2 and heavy crude oil) from the surface of water. They presented a common dynamic sorption method to compare the selected sorbents that was proved simple, rapid and efficient. According to their results polypropylene nonwoven web was the best material for oil spill cleanup in terms of oil sorption capacity. Bagasse of 18 to 45 mesh had a higher oil sorption capacity than 14 to 18 mesh bagasse and rice hull. The latter two sorbents had comparable sorption capacities. Importantly, sorption capacities of all sorbents except polypropylene nonwoven web were the same for heavy crude oil.

Annunciado et al. (2005) investigated the use of various vegetable fibers, namely mixed leaves residues, mixed sawdust, sisal, coir fiber, sponge-gourd and silk-floss as sorbent materials of crude oil. Their sorption tests with crude oil were conducted in various simulated conditions, deionized and marine water media, with and without agitation. Their research found that the sorption capacity of the fibers followed the general trend: silk-floss > sisal and sawdust > coir fiber > sponge-gourd > leaves residues and the sorption capacity might be further increased by reducing granulometry. The silk-floss fiber showed a rapid oil sorption and a very high sorption capacity of approximately 85 g of oil/g of sorbent (in 24 hr), high degree of hydrophobicity and low water uptake. The sorption capacity was around 8.5-12 times more than of two commercial products composed of peat sorb. They supposed that several of the low-cost vegetable fibers investigated might be used in dry environments, with variable sorption capacity. They examined the water uptake by the fibers with tests in dry conditions and distillation of the impregnated sorbent. They also used specific gravity measurements and buoyancy tests to evaluate the suitability of these fibers for the intended application. Their buoyancy tests indicated the inability of sisal, sponge-gourd and sawdust to be used in any water oil-spill conditions, whereas the leaves residues and the coir fiber might be adequate for marine environments.

Sayed and Zayed (2006) in their research investigated the effectiveness of solid waste sludge, garlic and onion peel as adsorbents in oil spill clean-ups. They examined the adsorption capacity of three different types of materials: a sludge which was mainly composed of calcium aluminum silicate and formed in water clarification and filtration and in dissolved air floatation units in petroleum refineries and thermal power stations, and garlic and onion peel as agricultural wastes. They investigated the characteristics of the crude oil and sludge by FTIR, X-ray fluorescence, X-ray diffraction, pour point and centrifuge instruments. Their results showed that the adsorption capacities of the chemically treated sludge with 30 μg/mL dodecyl benzene sulphonic acid, of the untreated sludge and the thermally treated sludge at 1200^{o}C were 2, 1.388 and 0.8 g/g respectively, while, garlic and onion peels had adsorption capacities of 0.385 and 0.455 g/g respectively. Their results were obtained by placing 0.6g crude oil on a saline solution (750 mL of 0.5 M NaCl at 30^{o}C) with different weights of the adsorbents for 90, 90, 90, 30 and 30 s for each, respectively. Since chemically treated and untreated sludge showed very efficient results when compared with results obtained in the literature where the results range from 1 to 4 g/g, Sayed and Zayed concluded that their materials are recommended to be recycled in oil spill clean-ups. Finally their experiments demonstrated that garlic and onion peels showed low oil uptake efficiency when compared to sludge.

Srinivasan and Viraraghavan (2008) evaluated the oil sorption capacities of walnut shell media. They countered the sorption capacity as the weight of oil picked up by unit weight of a sorbent. They estimated the initial oil pick-up by walnut shell media on pure oil and oil on aqueous medium. They conducted batch kinetic studies to evaluate the equilibrium time required by walnut shell media for sorbing oil. They observed that viscosity affected the sorption rates. Their research demonstrated that less viscous oil tended to penetrate into the pores at a faster rate while oils with a lower interfacial tension observed to be sorbed in larger quantities than the one with a higher interfacial tension. In their experiments, for pure oil medium, sorption capacities of 0.30 g/g, 0.51 g/g and 0.58 g/g were obtained for standard mineral oil, vegetable oil and DoALL Bright-Edge oil, respectively. Their results showed sorption capacities of 0.56 g/g, 0.58 g/g and 0.74 g/g for standard mineral oil, vegetable oil and DoALL Bright-Edge oil, respectively, for oil on aqueous medium. So, it is obvious that walnut shell media used for pure oil showed a higher recovery of oil in comparison to recovery in the case of oil on aqueous medium. Finally, they concluded that sorbed oil could be recovered from walnut shell media by applying mechanical pressure and that walnut shell media could be used as a sorbent for oil removal.

Nwokoma and Avene (2010) investigated the potential of using groundnut husk, agro-based waste, which is not only ubiquitous but indiscriminately littered around Nigerian urban areas, as an adsorbent in removal of oil spilled on water. The objective of their research was to study and evaluate the adsorption of crude oil from water using meshed groundnut shell as adsorbent. Their work included: determination of the loading or adsorption capacity, adsorption kinetics and isotherm. They converted groundnut shell, a waste generated in local vegetable oil processing plants, into a low cost adsorbent. This adsorbent was not only economical and biodegradable but could also be used for composting. The groundnut husk was treated and meshed to adsorb crude oil from water at various experimental conditions. Their investigations included the effects of sorbent dosage, particle size, contact time and temperature on the adsorption of crude oil. They concluded that meshed groundnut shell, especially less than 150μm, exhibited high affinity for oil adsorption with time. The optimum adsorption temperature range was found between 25-45°C. Their adsorption data indicated that a pseudo-second-order equation could be used to study the adsorption kinetics and the correlation coefficient of 0.9985 indicated that the sorption process was dominated by adsorption process. Their results demonstrated that crude oil removal by adsorption onto this abundantly available low cost and readily biodegradable material is feasible. They supposed that meshed groundnut shell adsorbent, with high affinity for oil and low water pick up, could be supposed to be oleophilic or hydrophobic.

Cojocaru et al. (2011) compared the performances of three peat-based sorbents in terms of oil sorption capacity, retention profile and oil removal efficiency. The three sorbents were extracted from different depths (0.5, 1 and 3 m). Their sorption experiments have been carried out employing three different oil samples: diesel oil, light liquid fuel and automotive oil. In their research they focused on three tests regarding oil sorption. First, they determined the initial retention capacity and retention profile using pure oil bath following the known standard methods for testing oil spill sorbents (ASTM F 726-99). Then, they deal with visual microscopy coupled to PC in order to identify the capillary phenomena inside of the peat fiber and to reveal their morphology. Finally, they deal with removal of oil slick by sorption in the presence of water column. They proposed an artificial neural network model for modelling and optimization of cleanup process dealing with sorption of oil product from water surface using the best sorbent originating from peat. Based on the results of their experiments, they concluded that the peat sorbent collected from the top surface of peat-land was the best material for oil spill cleanup in terms of oil sorption and retention capacity. Finally they demonstrated a three-layer feed-forward artificial neural network (ANN)-model with log-sigmoid transfer function at hidden layer and a linear transfer function at output layer in order to predict the efficiency of oil-slick removal from water surface. Their model showed a sufficient prediction of the experimental data with a satisfactory correlation coefficient of 0.9888 for three output variables, sorbent dosage, drainage time and initial thickness of oil slick.

5.2.2 Pretreated lignocellulosic materials

Sun et al. (2004b) examined the effect of tertiary amine catalysts on the acetylation of wheat straw for the production of oil sorption-active materials. In their study dried wheat straw was treated with acetic anhydride at 100 and 120^{o}C for 40-360 min with four tertiary amine catalysts (pyridine, 4-dimethylamino pyridine, N-methyl pyrrolidine, and N-methyl pyrrolidinone) or without catalyst in a solvent-free system, and the extent of acetylation was measured by weight percent gain. They found that 4-dimethylamino pyridine was the most effective catalyst of those studied. They performed FT-IR, CP-MAS and thermal studies to characterize the acetylated straw. They used FT-IR and CP-MAS studies to produce evidence for acetylation. They carried out thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) to study the thermal behavior of acetylated wheat straw and to compare it with the control. They found that the thermal stability of acetylated wheat straw was higher than the native straw. Their experiments showed that the acetylation significantly increased the hydrophobic properties of the straw. They tested the absorptivity of oil with machine oil. They estimated that the oil sorption capacities of the acetylated straws were much higher (1.2-2.9 times) than the commercial synthetic oil sorbents such as polypropylene fibres. Their results concluded that a total or partial substitution of commercial synthetic oil sorbents by acetylated wheat straw sorbents could be beneficial in the oil spill cleanup operation by improving the efficiency of oil sorption and by the incorporation of other advantages such as biodegradability.

Husseien et al. (2008) evaluated the oil adsorption using raw and carbonized barley straw. They also examined the behavior of raw barley straw and different commercial types on adsorption of oil. Their results revealed that the use of carbonized barley straw at 400^{o}C for 3 hours (hr) was found to be effective in recovering heavy oil spilled on water and in this condition the carbonized barley straw could be used as quality oil adsorbent. They established that thermal modification of the raw barley straw enabled reduction of water adsorption but had approximately negative influence on gas oil adsorption. They considered that all these treatments could improve the adsorptive properties of bioadsorbent. Even though, they studied the effect of sorption time on sorption capacity, the effect of sorption desorption and the reusability of carbonized and raw barley straw in pad form.

Ibrahim et al. (2009) modified chemically barley straw and evaluated its removal capacity of emulsified oils from aqueous solution. The chemical modification was performed using NaOH and a cationic surfactant, hexadecylpyridinium chloride monohydrate (CPC). Their investigation demonstrated the surfactant modified barley straw exhibiting good performance to adsorb emulsified oil from aqueous solution. The adsorbent characterizations proved the successful impregnation of CPC onto raw barley straw. Their batch study also revealed that the adsorption was a function of particle size and pH. The adsorption capacity was reduced when the oil solution was in strong acidic condition (i.e. pH 2) and reached the maximum at pH around neutral (pH 6 and 8). They demonstrated Langmuir isotherm to provide the best correlation for the equilibrium adsorption data and its adsorption capacity was found slightly higher for canola oil than standard mineral oil. Their kinetic experiment revealed that adsorption of oil was rapid at initial stage followed by slower phase where equilibrium uptake was achieved. Due to abundant availability and easy modification at relatively low cost, the application of the surfactant modified barley straw showed a promising alternative method for emulsified oil wastewater treatment.

Ibrahim et al. (2010) prepared a surfactant modified barley straw (SMBS), characterized by several physicochemical methods and tested as an effective sorbent for emulsified canola oil removal from aqueous solution. Their major efforts were summarized as follows: characterization of SMBS based on FT-IR spectra, BET surface area and measurements of surface acidic and basic groups proved the existence of hexadecylpyridinium chloride monohydrate (CPC) on the surface of barley straw. Desorption of CPC from SMBS was higher in the aqueous acid solution than in deionized water. This indicated that the strong bonding between CPC and straw surface with ion exchange was the major mechanism of CPC adsorption on the barley straw. Their kinetic studies revealed that oil adsorption on SMBS was rapid and equilibrium could be reached within 40 min. They found that oil adsorption was depended on adsorbent dosage, particle size, solution pH and temperature. The oil adsorption would be higher at low dosage, smaller particle size, pH around 6-8 and temperature of 20-40^{o}C. Finally, they supposed that oil adsorption on SMBS would be better represented by the Langmuir isotherm better than Freundlich model and they found that maximum adsorption capacity was 576.0 mg/g.

Hussein et al. (2008) examined the oil adsorption capacity and the physical properties of carbonized pith bagasse. They also investigated the water adsorption properties of the carbonized pith bagasse to explore their practical applications in treating oil spills within water. They supposed that among all the existing techniques used for oil treatment, sorption is a cheap, simple and effective technique; and among the various sorbents used pith bagasse appeared to be the most attractive material in terms of cost, versatility and abundance. In their experiments, they carbonized pith bagasse in a stainless steel tube for different temperatures ranging from 200 to 600^{o}C and for different heating periods from 1 to 3 hr. They used gas oil, 1-day and 7-day weathered heavy Arabian crude oil to test the carbonized pith bagasse. They found that sorption capacity and porosity of any activated carbon depended largely on carbonization conditions, morphology and physical state of pith bagasse. They proved (from the results of SEM micrographs and adsorption properties of carbonized pith bagasse) that carbonization played the major role in porosity development of any type of raw material. They suggested that the increasing in the oil sorption capacity as temperature increased was attributed to the formation of many small pores in which oil was sorbed as they demonstrated in the electro scanning micrographs. They found that carbonization of pith bagasse improved the oleophilic and hydrophobic properties; and that the best carbonization conditions were at 300^{o}C for 2 hr where the % yield was efficient and sorption capacity increased. Finally, they concluded that higher temperature decreased the yield of activated carbon.

Angelova et al. (2001) examined the influence of the density of oil products and the apparent density of the carbonized rice husks (obtained by pyrolysis, carried out at a temperature of 480^{o}C) upon the adsorption capacity, mechanism and the sorption kinetics. They also determined the role of surface functional groups on the adsorption characteristics of the above mentioned material and they studied it as adsorbent for purification of pollutions caused by oil and oil products. They determined the amount and composition of the fluids, dispersed on the surface of the carbonized rice husks, by applying extraction and gas chromatography-mass spectrometry method (GC-MS). They characterized the material with respect to the specific surface area by BET method and mercury porosimetry. In their experiments they estimated the adsorption capacity of the pyrolyzed rice husks in respect of water, oil and petroleum products with different densities. They found that their material had very satisfactory buoyancy characteristics, high oil sorption capacity and high hydrophobicity. They suggested that the dependence between the bulk density of the adsorbent and the height of penetration of the oil in it for a specified time was inversely proportional. They mentioned that the height of penetration of the sorbate in the sorbent layer depended on the density of the liquid phase. They estimated that the changes of the adsorption rate for the various oil products could be described by hyperbolic dependence. They concluded that a correlation between surface functional groups and morphology of the adsorbent and adsorption properties of the material was created; and that their research provided the basis for development of a new environmental material with optimal characteristics, providing efficient adsorption of oil and oil products from aqueous medium. Finally, we could suppose that the aim of their study was to determine both the optimal height of the layer of adsorbent in the course of decontamination of the water from oil and oil products spills, as well as the time interval, needed to reach adsorption-desorption equilibrium.

Sun et al. (2002) investigated the effect of a solvent-free system on rice straw acetylation at different times and temperatures with or without catalysts and the characterization of the rice straw as a natural sorbent in oil spill cleanup. In their experiments they used as catalysts 4-Dimethylaminopyridine (DMAP), pyridine, N-methylpyrrolidine (MPI), and N-methylpyrrolidinone (MPO). They found that DMAP was the most effective catalyst of those studied. They investigated the reaction by performing Fourier transform infrared (FT-IR) and solid-state carbon-13 nuclear magnetic resonance spectroscopy. They studied the thermal behavior of acetylated rice straw to compare it with the control by carrying out thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). They tested the adsorption property of the acetylated straw using machine oil. They estimated that the acetylated straw was significantly hydrophobic and did not get wet with water, thereby offering potential for the better utilization of a cheap waste material as natural sorbent in oil cleanup. They suggested that the oil sorption capacities of the acetylated straws were much greater than those of the synthetic sorbents such as polypropylene fiber. Therefore, the acetylation of rice straw might prove to be technically feasible and environmentally acceptable. Finally, they concluded that this technology could have useful applications in the area of oil spill cleanup by natural and biodegradable sorbents.

Kumagai et al. (2007) examined the oil adsorption capacity, the chemical composition and the porosity of carbonized rice husks (agricultural waste). They also investigated the water adsorption properties of the carbonized rice husks to explore their practical applications in treating oil spills within water. In their research, they pyrolyzed raw and refined (defiberized) husks in a vacuum (500 Pa) at 300-800^{o}C for 1 to 5 hr to impart superior properties for use as an oil adsorbent. They evaluate the amount of A-heavy and B-heavy oils adsorbed on the carbonized rice husks. They estimated that the oil adsorption was dependent on the type of oil. Their results demonstrated that rice husks refined and then pyrolyzed at 600-700^{o}C (1.0 g) adsorbed > 6.0 g of B-heavy oil and < 1.5 g of water, which indicated their usefulness as an adsorbent for oil spill cleanup. They found that the refining process contributed to an improvement in the oil adsorption capacity, while the carbonization time (at

600^{o}C) had only a minor influence. They concluded that the residual fluid components in the carbonized rice husks, rather than their porosity, were closely related to oil adsorption capacity while the formation of oleophilic fluid by the carbonization process and structural change via the refining process, rather than by capillary action, was important mechanism in enhancing the oil adsorption capacity of rice husks.

Vlaev et al. (2011) studied the structure of black rice husk ash (BRHA) and white rice husks ash (WRHA) obtained by thermal degradation of raw rice husks on a pilot plant fluidized-bed reactor and the possibilities to use these products as an adsorbent for cleaning spilled oil, oil products or bilge water. They supposed that moreover the ships produce a large amount of oily wastewater such as bilge water (a difficult waste water to treat as it contains seawater, particulates, used oils and detergents) which needs to be treated prior to being discharged. They reported that the micro and ultrafiltration are often the methods of choice to treat this water while the pretreatment of this oily wastewater prior to ultrafiltration is desirable, as the used oils and particulates can block the feed channels of the ultrafilters spiral and hollow fiber modules. In this reason, they mentioned that at the last time different hybrid adsorbents with high adsorption capacity and appropriate porous structure are used. Their study was an attempt to establish the possibilities to obtain BRHA and WRHA via pyrolysis of raw rice husks in a pilot plant fluidized-bed reactor at different conditions. The sorbent materials produced from their research were used as adsorbents for purification of crude oil and diesel fuel from water surfaces and for cleaning of bilge water. The products obtained from their experiments were characterized using X-ray diffraction patterns, scanning electron microscopy, FT-IR spectroscopy, thermal analysis, and low temperature nitrogen adsorption. They studied the kinetics and they determined the adsorption capacities of crude oil and diesel fuel at different temperatures as well as some hydrocarbons at 298 K onto BRHA and WRHA by using batch adsorption technique. From their research was established that BRHA had been higher adsorption capacity than WRHA and at a given temperature, BRHA sorbed more crude oil than diesel fuel. Their results showed that the material studied had high adsorption capacity and low cost and might successfully be used as an effective adsorbent to cleanup of bilge water and spills of oil and oil products in water basins. They suggested that, because the saturated BRHA with crude oil, diesel fuel or different hydrocarbons were characterized with high calorific, they could be burned in incinerators, industrial ovens or steam generators. By this way the researchers attained not only ecological but also economical effect.

Sun et al. (2004a) investigated the acetylation of sugarcane bagasse with acetic anhydride by using N-bromosuccinimide (NBS) as a catalyst in a solvent free system as a method to obtain fibres with high hydrophobic properties under mild conditions. They measured the extent of acetylation by weight percent gain (WPG), which varied from 2.1% to 24.7% by changing the reaction temperature (25-130^{o}C) and duration (0.5-6.0 hr). They found that NBS was a novel and highly effective catalyst for acetylation of hydroxyl groups in bagasse. They estimated that at a concentration of 1% of the catalyst in acetic anhydride, a weight percent gain of 24.7% was achieved at 120^{o}C for 1 hr, compared with 5.1% for the un-catalyst reaction under the same reaction condition. They used FT-IR and CP-MAS studies to produce evidence for acetylation. They supposed that the thermal stability of the products decreased slightly upon chemical modification, but they did not observed significant decrease in thermal stability for WPG>= 24.7%. They found that the acetylation significantly increased hydrophobic properties of the bagasse. Their experiments showed that the oil sorption capacity of the acetylated bagasse obtained at 80^{o}C for 6 hr was 1.9 times higher than the commercial synthetic oil sorbents such as polypropylene fibres. They finally concluded that the oil sorption-active materials examined in their research could be used to substitute non-biodegradable materials in oil spill cleanup.

Banerjee et al. (2006a) demonstrated the efficacy of surface modification of sawdust by fatty acids (oleic acid, stearic acid and decanoic acid) and vegetable oils (castor oil or mustard oil). Their research aimed at evaluating the possibility of removing oil and weathered oil contaminated seawater (WOCS), using sawdust, a waste from the timber industry. They supposed that though abundantly distributed sawdust had a major disadvantage, that it very quickly absorbed water and hence, the oil sorption capacity was reduced considerably. They mentioned that the sorption properties of sawdust could be significantly improved by making the surface hydrophobic. They discussed a new approach in their study, the use of fatty acids and vegetable oils to change the surface character of sawdust from polar to organophilic. They found that the sorption of seawater contaminated with crude oil and also weathered oil was greatly enhanced by the surface modification.

Their results showed that the sorption behavior of sawdust was greatly enhanced when modified with fatty acids and vegetable oils. Oleic acid grafted sawdust (OGSD) had the best sorption capacity for crude oil as well as weathered oil and so was the better candidate compared to conventional sorbents. Moreover, contrary to polymers which are used during oil spillage, sawdust was respectful to the environment. It was biodegradable and would not lead to supplementary pollution, contrarily to polymers. They also observed that when the light oil fraction of the crude oil increased, the sorption capacity was enhanced. They concluded that this was an added advantage of their material in contrast to other sorbents like straw, which cannot retain large proportion of light oils. They finally estimated that fatty acid and vegetable oil modified sawdust samples are potential sorbents for oil spillage.

Sathasivam and Harris (2010) evaluated the use of banana trunk fiber (BTF) for sorption of spilled oil on aqueous media. Since BTF tends to also absorb water, its oil sorption capacity may be drastically reduced. Thus, esterification reaction was introduced to increase the hydrophobicity of the fibers. Their primary objectives were to: modify BTF with oleic acid, stearic acid, castor oil, and palm oil, and evaluate oil sorption capacity of the resulting fibrous materials. They proved that oil sorption capacity of modified BTF with oleic acid, stearic acid, castor oil, and palm oil increased markedly as compared with that of the unmodified fibers. Among all the modified BTF, oleic acid-grafted BTF was found to have the best sorption capacity for engine oil, dissolved organic compounds in weathered oil, and light oil fractions. Furthermore, they found that the reusability of the modified BTF was impressive as the material was able to retain its original efficiency to sorb oil for at least three repeated cycles. They concluded that sorption of engine oil and dissolved organic compounds in weathered oil fitted best in the Freundlich isotherm and pseudo second-order kinetic models.

Adsorption isotherms

The adsorption isotherm yields the equilibrium temperature curve, essential adsorption information and guidelines for selecting methods of adsorption and partition (Hsu and Pan, 2007). Equilibrium relationship between the sorbents and the sorbates are described by sorption isotherms which gives the capacity of a sorbent for a sorbate (Ho, 2006). As isotherm tests weren't executed in this study, literature survey shows that equilibrium isotherm equations are used to describe experimental sorption data.

Among several models that have been published in the literature to describe experimental data of adsorption isotherms Langmuir, (Langmuir, 1916) and Freundlich, (Freundlich, 1906), are the most frequently used models (Banerjee et al., 2006; Lin and Juang, 2009; Ibrahim et al., 2009; Ibrahim et al., 2010; Sathasivam and Haris, 2010; Nwokoma and Anene, 2010; Thompson et al., 2010; Syed et al., 2011; Husin et al., 2011; Sidik et al., 2012; Nafaty et al., 2013). The equation parameters and the underlying thermodynamic assumptions of these equilibrium models often provide some insight into both the sorption mechanism and the surface properties and affinity of the sorbent. The Temkin, (Temkin and Pyzhev, 1940), isotherm model is also used as literature survey shows (Sathasivam and Haris, 2010; Syed et al., 2011; Sidik et al., 2012).

The Freundlich isotherm, describes the equilibrium on heterogeneous surfaces, does not assume monolayer capacity and is given by the following equation:

$$q = K_F \cdot (C_e)^{\frac{1}{n}} \tag{5.1}$$

where: q is the amount adsorbed per unit mass of the adsorbent (mg g^{-1}), C_e is the equilibrium concentration of the adsorbate (mg L^{-1}) and K_F, n are the Freundlich constants related to adsorption capacity and intensity, respectively. Eq. (5.1) in logarithmic form gives:

$$\log q = \log K_F + \frac{1}{n}\log C_e \tag{5.2}$$

The Langmuir isotherm, describes the surface as homogeneous assuming that all the adsorption sites have equal solute affinity and that adsorption at one site does not affect the adsorption at an adjacent site and is given by the following equation:

$$q = \frac{K_L q_m C_e}{1 + K_L C_e} \tag{5.3}$$

or

$$\frac{1}{q} = \left(\frac{1}{q_m}\right) + \left(\frac{1}{K_L \cdot q_m}\right) \cdot \left(\frac{1}{C_e}\right) \tag{5.4}$$

where: K_L is the Langmuir constant related to the energy of adsorption ($L.mg^{-1}$) and q_m the amount adsorbed per unit mass of the adsorbent (mg g^{-1}) when saturation is attained. The parameters K_L and q_m can be obtained either by plotting 1/q versus $1/C_e$ or by non-linear regression analysis. From the technical point of view, parameter q_m is the most important parameter representing the maximum adsorption capacity of the adsorbent.

The Temkin isotherm model, is given by the following equation:

$$q = \frac{RT}{b_T}\ln(A_T C_e) \text{ or } q = B_T \ln(A_T C_e) \text{ or } q = q_m \ln(K_L C_e) \qquad (5.5)$$

where: R=0.008314 kJ mol^{-1} K^{-1}, T is the adsorption temperature in K, $K_L=A_T$ in L mg^{-1} and $q_m=B_T=RT/b_T$ in mg $^{g-1}$. In linearized form eq. (5.5) is as follows:

$$q = a_T + q_m \ln(C_e) \qquad (5.6)$$

where: $a_T=q_m \ln(K_L)$.

The Freundlich and Langmuir parameters of adsorption isotherms for various adsorbents according to the literature are presented in Table 5.1.

Table 5.1 The Freundlich and Langmuir parameters of adsorption isotherms for various adsorbents according to the literature

Adsorbent	Oil Type	Freundlich		Langmuir		Reference
		K_F [(mg g^{-1}) (L mg^{-1}) $^{1/n}$]	n	q_m (mg g^{-1})	K_L (L mg^{-1})	
Activated carbon	Phenol	2.60	0.88			Mukherjee et al. (2007)
Bagasse ash	Phenol	0.23	0.66			Mukherjee et al. (2007)
Banana peel	Crude oil	0.06	1.33	-6.82	$1.237 \cdot 10^{-5}$	El-Nafaty et al. (2013)
Banana pseudostem fibers	Palm oil	38.29	2.88	169.00	0.01	Husin et al. (2011)
Banana trunk fibers (unmodified)	Engine oil	28.64	1.28	149.25	0.25	Sathasivam and Haris (2010)
Banana trunk fibers (oleic acid-treated)	Engine oil	250.26	2.52	400.12	0.48	Sathasivam and Haris (2010)
Banana trunk fibers (stearic acid treated)	Engine oil	202.55	1.61	434.78	0.96	Sathasivam and Haris (2010)
Banana trunk fibers (castor oil-treated)	Engine oil	234.56	2.60	333.33	0.75	Sathasivam and Haris (2010)
Banana trunk fibers (palm oil-treated)	Engine oil	138.10	1.32	476.90	0.44	Sathasivam and Haris (2010)
Banana trunk fibers (unmodified)	Weathered oil	7.23	1.23	312.50	0.02	Sathasivam and Haris (2010)
Banana trunk fibers (oleic acid-treated)	Weathered oil	108.79	5.59	212.77	0.38	Sathasivam and Haris (2010)
Banana trunk fibers (stearic acid treated)	Weathered oil	24.11	1.57	263.16	0.08	Sathasivam and Haris (2010)
Banana trunk fibers (castor oil-treated)	Weathered oil	32.57	2.47	166.67	0.10	Sathasivam and Haris (2010)

Banana trunk fibers (palm oil-treated)	Weathered oil	25.54	2.37	142.86	0.09	Sathasivam and Haris (2010)
Barley straw (NaOH treated)	Canola oil	112.10	4.76	613.30	0.01	Ibrahim et al. (2009)
Barley straw (NaOH treated)	Standard mineral oil	165.00	5.94	584.20	0.01	Ibrahim et al. (2009)
Barley straw (surfactant modified)	Canola oil	84.40	4.25	576.00	3.87×10^{-3}	Ibrahim et al. (2010)
Fly ash	Crude oil	41.11	4.18			Banerjee et al. (2006b)
Fly ash	Weathered oil	0.06	1.29			Banerjee et al. (2006b)
Fly ash (methylammonium treated)	Crude oil	57.54	3.36			Banerjee et al. (2006b)
Fly ash (methylammonium treated)	Weathered oil	0.22	1.11			Banerjee et al. (2006b)
Nano-silica (hydrophobic)	Gasoline	1.02	0.07	1.16	-97.57	Syed et al. (2011)
Nano-silica (hydrophobic)	Diesel oil	0.94	0.07	1.18	-172.66	Syed et al. (2011)
Oil palm leaves (lauric acid modified)	Crude oil	1.72	1.39	1.95	0.16	Sidik et al. (2012)
Paper mill sludge (activated with $ZnCl_2$)	Phenol	0.44	1.18			Khalili et al. (2002)
Powdered activated carbon	Phenol	1.07	2.70			Mukherjee et al. (2007)
Raw rice husks	Crude oil	1.01	3.55	1.79	-15.50	Thompson et al. (2010)
Raw rice husks (acetylated at optimum conditions)	Crude oil	4.03	2.60	8.26	1.98	Thompson et al. (2010)
Raw rice husks (acetylated with optimum sorption capacities)	Crude oil	4.11	2.20	10.31	2.11	Thompson et al. (2010)
Sawdust	Crude oil	2.89	5.59			Banerjee et al. (2006a)
Sawdust	Weathered oil	0.11	0.78			Banerjee et al. (2006a)
Sawdust (oleic acid treated)	Crude oil	4.57	3.48			Banerjee et al. (2006a)
Sawdust (oleic acid treated)	Weathered oil	0.05	0.57			Banerjee et al. (2006a)
Wood charcoal	Phenol	0.17	1.08			Mukherjee et al. (2007)

5.3 Use of non lignocellulosic materials as oil adsorbents

In the previous subchapter the use of lignocellulosic materials as oil adsorbents was performed. In this subchapter the use of other, non lignocellulosic materials as oil adsorbents will be introduced. Literature survey shows that many researchers used numerous untreated and pretreated non lignocellulosic materials as adsorbents for oil spill cleaning. Some of the above mentioned materials are: organo-clays (Carmody et al., 2007), exfoliated graphite (Toyoda and Inagaki, 2003; Tryba et al., 2003), expanded perlite (Bastani et al., 2006), activated carbon (Inagaki et al., 2002), kapok (Choi and Moreau, 1993; Lim and Huang, 2007a; Lim and Huang, 2007b; Abdullah et al., 2010), cocoon (Moriwaki et al., 2009), natural wool fibers (Rajakovic et al., 2007), recycled wool based nonwoven material (Rajakovic et al., 2007; Radetic et al., 2008), cotton fiber, kenaf bast fiber, kenaf core fiber, moss fiber (Lee et al., 1999), cotton treated and raw (Deschamps et al., 2003), sepiolite (Rajakovic et al., 2007), waste tire powder (Lin et al., 2008) and polyurethane foams (Li et al., 2012).

5.3.1 Untreated non lignocellulosic materials

Toyoda and Inagaki (2003) studied the behavior of sorption of heavy oils into exfoliated graphite samples with different bulk density by using four grades of heavy oil with different viscosity. The principal purposes of their study were to examine the recovery of spilled or dispersed heavy oils by using carbon materials and recycle of both heavy oils and carbon materials. They found that maximum sorption capacity of exfoliated graphite was 83 g of A-grade heavy oil per 1 g of the exfoliated graphite with low bulk density as 6 kg/m^3 and also its sorption occurred very rapidly, within 1min at 25C^o. Their research showed that the sorption capacity depended strongly on bulk density and total pore volume of exfoliated graphite with increasing bulk density from 6 kg/m^3 and higher sorption capacity decreases markedly. Also, they found that the time to reach maximum sorption, as well as sorption capacity, of an exfoliated graphite depended strongly on grade of heavy oil; a large amount of heavy oils with low viscosity (A-grade and crude) was sorbed in a short time, but oils with high viscosity (B and C-grades) needed a long time although sorbed amount was relatively small. They assumed that heavy oils sorbed into exfoliated graphite could be recovered by a simple filtration under mild pressure with the recovery ratio of about 70% and could not be differentiated from the original in the bases of molecular weight values and the content of various hydrocarbons, indicating that the recovered oils had no problems for recycling. Their study revealed the possibility for practical application of high sorption capacity of exfoliated graphite by packing it into a bag if the material of the bag and the way of picking up from heavy oil were properly selected. Recycling of exfoliated graphite for sorption of heavy oil was found to give marked reduction of sorption capacity.

Bastani et al. (2006) studied the sorption capacity as well as sorption kinetics of oil onto four (A_0, A_1, A_2 and A_H) different expanded perlites with different physical and surface properties. They used Scanning Electron Microscopy (SEM) images for the expanded perlite to show that these four types of perlite were different in their porous space. In order to meticulously measure the amount of oil to be sorbed onto the adsorbents used in their study both static and dynamic methods in bench scale were employed. It would be worth noting that the adsorbent, i.e., perlite could spread on the oil and float on the surface thanks to its low density. The variation of the amount of oil sorbed onto the adsorbents in relation to time was recorded and the weight of adsorbent was monitored at each specified time. Their experimental results showed that grain sizes with high surface area could sorb oil that was spread on water surface. It should be also stressed that their experiments were triplicated and their results reported were the average. Also kinetic studies for sorption of oil at ambient temperature using the expanded perlite were performed. Their results obtained were correlated with the first order, second order sorption kinetics as well as the intra-particle diffusion models. Their results showed that the second order kinetic model studied could more accurately correlate the experimental data generated than the first order sorption kinetic and the intra-particle diffusion models.

Choi and Moreau (1993) compared oil sorption capacities of various natural and man-made fibrous sorbents in a simulated seawater bath containing oil. The purpose of their study was to investigate sorption mechanisms of various fibers. Their research found that natural sorbents such as milkweed, kapok, cotton, and wool showed higher sorption capacities than man-made sorbents such as polyester, polypropylene, viscose rayon, nylon 6, nylon 66, and acetate. Sorption capacities of the natural sorbents were over 30 g of oil/ g of fiber. Their analyses of sorption mechanisms using an environmental scanning electron microscope revealed that an oil deposit disappeared from the fiber surface after a certain time interval in milkweed, kapok, and cotton. They suggested that the sorption of oil in these fibers occurred through capillary action, probably due to their hollow lumens. Contrarily, adsorption, a surface phenomenon, would be the most prominent mechanism for oil sorption of wool fibers due to large amounts of surface wax, irregular scaly surfaces, and crimp. In their work effects of both adsorption and absorption were shown in the oil sorption of man-made fibers, depending upon the type and shape of the sorbent. Dumbbell-like oil deposits were seen on the fiber surface in certain oleophilic man-made fibers, because of a partial wetting of oil on the fiber surface. They concluded that for some hydrophilic man-made fibers such as polyvinyl alcohol and copolymer of isobutylene-maleic anhydride, the physical configuration of the fiber was a decisive factor in determining oil sorption capacity of the sorbents.

Moriwaki et al. (2009) investigated the utilization of silkworm cocoon waste, such as pierced or stained cocoons, as a low cost sorbent material for the removal of motor and vegetable oils from water. In general, the silkworm cocoon is expensive. However, most of the pierced cocoons or very dirty cocoons of the silkworm are discarded as industrial wastes, and could be obtained as a low cost material. They estimated that the silkworm cocoon had the properties of a slow biodegradability and the shell of the silkworm cocoon contained wax and showed hydrophobic property; important preconditions for an efficient oil sorbent. In their experiments, they milled the silkworm cocoon waste without removal of sericin, and they used the obtained flocculate material as a sorbent for oil in their study. They evaluated the oil-sorption capacity, rate and reusability of the material. Their results showed the high sorption capacity of the silkworm cocoon waste sorbent (42-52 g of oil/ g of sorbent for motor oil and 37-60 g of oil/ g of sorbent for vegetable oil). They supposed that the oil sorbed onto the material could be recovered by squeezing the sorbent, and the squeezed material showed an oil-sorption capacity over 15 g of oil/ g of sorbent. They concluded that the material showed a high performance as a low cost and environmental friendly sorbent for the removal of oil from water.

Rajakovic et al. (2007) investigated the efficiency of different sorbent materials for oil removal from wastewater. They examined two types of sorbents: organic {loose natural wool fibers (NWF) and recycled wool based nonwoven material (RWNM)} and inorganic (sepiolite). Their study aimed to analyze and compare these types of sorbents’ performance and efficiency. In their experiments, sorption was carried out in continuous tubular contractor (initial oil concentration of 1,511 mg/dm^3) and batch tank (initial oil concentration of 5,066 mg/dm^3). They found that wool-based sorbents showed higher sorption capacity (5.56 g/g for NWF and 5.45

g/g for RWNM) compared to sepiolite (0.19 g/g) in case of sorption in batch tank. On sorption in continuous tubular contractor they suggested that volume of oily wastewater strongly affected oil removal. Their results indicated that the combination of extractive-gravimetric and FTIR spectrophotometric methods could be recommended for precise determination of oil concentration, being suitable as a controlling toll for oil detection.

Radetic et al. (2008) investigated the efficiency of recycled wool-based nonwoven material (RWNM) for the removal of a wider range of oils (diesel, fuel, crude, base, vegetable and motor oil) from water. They determined RWNM's oil sorption capacity, oil retention, possible reusability as well as its buoyancy in static and dynamic conditions, to evaluate the potential use of RWNM for oil removal. They examined the sorption capacity of the material in water and in oil without water and their results showed high sorption capacity of recycled wool for different kinds of oil. They also found that this sorbent exhibited excellent buoyancy after 24 hr of sorption as well as a good reusability since the decrease in sorption capacity did not exceed 50% of the initial value after five sorption cycles in oil without water. To assess a possible mechanism of oil sorption on RWNM, they carried out in situ environmental scanning electron microscopy (ESEM) analysis. They concluded that RWNM could be used for the sorption of different types of oil particularly due to high sorption capacity in water and oil without water. They also found that retention of their studied oils on sorbent was satisfactory except for the motor oil and the sorbent showed satisfactory buoyancy in static and dynamic conditions and did not sink even after 24h in aquatic medium. Their SEM's images revealed no fiber fibrillation that could had occurred during the production of the material, although they observed some fiber damage. Their ESEM's images suggested that oil sorption on recycled wool was likely to be governed by adsorption. Finally, they concluded that efficient oil sorption properties, excellent reusability and biodegradability make RWNM a sorbent material viable alternative to commercially available synthetic sorbents.

Lee et al. (1999) compared the oil sorption capacities of cotton fiber, kenaf bast fiber, kenaf core fiber, and moss fiber after refining, extraction, and reduction in particle sizes. Their tests were conducted on diesel oil in a pure form. Cotton fiber showed the highest capacity, followed by kenaf core and bast fibers.

Wetting, extraction, and reduction in particle size all contributed to the changes in sorption capacity. They found that the most significant change was due to the reduction in particle sizes of cotton and kenaf bast fibers; however, the kenaf core was not affected. Typically, lignocellulosic fibers are hydrophilic resulting in low capacity to sorb oil. They supposed that these hydrophilic fibers must be converted to hydrophobic fibers to improve the oil sorption capacity. Cotton exhibited the highest capacity for oil sorption among the fibers examined. This sorption was due to the large amount of wax on the fiber surface, the hollowed surface, and the larger, non collapsing lumen of the fiber. Solvent extraction slightly reduced the oil sorption characteristics of the cotton. Presoaking in water and reduction in particle size slightly changed the oil sorption capacity of kenaf core. On the other hand, they found that a reduction in particle size reduced the oil sorption capacity of kenaf bast and cotton. Finally, they assumed that the surface area, pore size, oil content, shape, and strength of fibers were factors that affected oil sorption capacity.

Lin et al. (2008) examined the possibility of applying waste tire powder as a sorbent for the recovery of spilled oil. They mentioned that the tire rubber was flexible and had hydrophobic (oleophilic) characteristics, making it an efficient candidate as an oil adsorbent. Their results indicated that 2.2 g of motor oil could be adsorbed to each gram of 20 mesh tire powder. They estimated that due to its elastic property, waste tire powder was re-usable for over 100 times without decreasing its oil absorption efficiency. Therefore, they found that at least 220 g of motor oil could be recovered per gram of waste tire powder, which was very competitive to commercial sorbents. Their experiments showed that sorption efficiency increased as the tire powder particle size decreased, and decreased as the environmental temperature increased. They suggested that when applying the waste tire powder to oil slicks on seawater, the oil sorption was shown to be higher than if it was on fresh water. They made efforts to enhance the waste tire powder’s oil sorption efficiency. Their results indicated that the highest efficiency was obtained when the waste tire powder was pre-cleaned by n-hexane, followed by water cleaning > un-cleaned > dishwashing liquid cleaned > seawater cleaned. They estimated that compared to a commercial oil sorbent, their experimental results indicated that waste tire powder was economically more feasible, if it was re-used for 100 times. Finally, they concluded that more efforts should be encouraged to enhance the waste tire powder’s oil sorption capacity without decreasing its re-usable characteristics. If the proposed ideal of their research was applicable to utilize tire particle as oil sorbent in oil spill recovery, not only will it benefit to the oil pollution prevention, but will also bring profit to the scrap tire recycling industry.

5.3.2 Pretreated non lignocellulosic materials

Carmody et al. (2007) tested organo-clays synthesized by the ion exchange of sodium in Wyoming Na-montmorillonite with three surfactants: octadecyltrimethylammonium bromide (ODTMA), dodecyldimethylammonium bromide (DDDMA) and di(hydrogenated tallow) dimethylammonium chloride, for hydrocarbon adsorption. Using diesel, hydraulic oil, and engine oil they evaluated the effectiveness of the sorbent materials for a range of hydrocarbon products that were likely to be involved in land based oil spills. They found that the hydrocarbon sorption capacity of the organo-clays was depended upon the materials and surfactants used in the organo-clay synthesis. Greater adsorption was obtained if the surfactant contained two or more hydrocarbon long chains. Thus, they supposed that the use of organo-clays for cleaning up oil spills is feasible due to its many desirable properties such as high hydrocarbon sorption/ retention capacities and hydrophobicity. The negative effects of the use of organo-clays for oil-spill cleanup were the cost, the biodegradability, and recyclability of the organo-clays. Thus, the aim of their study was to evaluate the performance of organo-clays for cleaning up oil spills by: assessing the performance of commercially available sorbents in current use, developing improved clay-based sorbents (organo-clays) for use in oil spill applications, and ranking overall sorbent performance on the basis of the sorption capacities and other performance criteria (i.e., environmental, cost, and end use attributes).

Tryba et al. (2003) used commercial exfoliated graphite for checking its sorption capabilities for removing engine oil and dyes from wastewater. In their work, the effect of oxidation of exfoliated graphite on sorption of oil and some organic substances dispersed in water was examined, in order to check the applicability to simultaneous removal of all organic contaminants, including oil, in wastewater. Although their experiments did not gave very high sorption capacity values for oil, they found that slight oxidation of exfoliated graphite in the air at 400^{o}C was effective to improve adsorption capacity for dyes, methylene blue and methyl orange dissolved into water. Their study also showed that exfoliated graphite treated in HNO_3 reduced all sorption capacities for engine oil and dyes. They revealed a possibility for simultaneous removal of oil and dyes dispersed in wasted water. They concluded that considering the fact that macropores existing both in the particles of exfoliated graphite and among the particles were responsible for oil sorption and micropores in the particles for the adsorption of dyes, there would be the possibility to remove dispersed oil and dissolved dyes simultaneously from wastewater by optimizing the mixing conditions, not rigorous stirring but giving enough contact between wastewater and exfoliated graphite.

Inagaki et al. (2002) determined the sorption capacity for heavy oils, less viscous A-grade and more viscous C-grade on fibrous carbon materials, including activated carbon. Their work focused on recovery and recycling of spilled oils using carbon materials; the sorption capacity of various carbon fibers was measured and compared with those of exfoliated graphite and carbonized fir fibers which were studied in their previously research. They found that the sorption capacity depended strongly on their materials bulk density; the correlation was the same as found on exfoliated graphite and carbonized fir fibers. They observed excellent recycling performance on carbon fiber felts, though sorption capacity was found not as high as on exfoliated graphite and carbonized fir fibers. They studied in detail, by applying not only filtration and solvent washing but also centrifugation and squeezing, their recycling performance for two grades of heavy oils with different viscosity. Their experiments showed that by filtration under suction, about 90% of sorbed A-grade heavy oil could be recovered and no decrease in sorption capacity was detected even after eight cycles. They estimated that by washing with solvents, *n*-hexane for A and C-grade oils and A-grade oil for C-grade oil, almost 100% recovery with no marked reduction in sorption capacity was found for each cycle. They supposed that for the felts of PAN-based carbon fibers, rather severe operations for oil recovery, centrifugation and squeezing with twisting, could be applied without pronounced decreases in sorption capacity and recovery ratio. They concluded that although the sorption capacity was not so high, about 20 kg/kg, carbon fiber felts were found to have certain advantages in excellent recycling performance.

Lim and Huang (2007a and 2007b) examined kapok performances, as untreated and solvent-treated fibers, in deep-bed filtration of oily water containing 2.5% diesel, in their study. Kapok fiber, an agricultural product, contains waxy material that contributes to its hydrophobic-oleophilic characteristics. They used ethanol and chloroform as solvents and low viscosity oil (diesel oil) in their research. They evaluated the filtration performance through measurements of column breakthrough time, filtration rate, filtrate quality and the amount of oil retained by the filter column at breakthrough under a constant vacuum pressure. They found that the kapok fibers, both at their natural state and after solvent treatments, demonstrated excellent oil/ water separation and filtration; oil was retained while water was filtered through the kapok fiber column. They supposed that the filtrate quality, in terms of turbidity and percent oil removal, appeared to be unaffected by the solvent treatment of the kapok fiber. Their results revealed that the oil removal efficiencies consistently exceeded 99%. However, the filter column packed with solvent-treated kapok fibers showed premature breakthrough of the oily influent and produced less filtrate than that by the untreated kapok. The filter column packed with the solvent-treated kapok also retained less oil compared to the untreated kapok, and as a result, a quarter of the filter pore volume was not wetted even after breakthrough. They concluded that this could be the main cause for the premature breakthrough of the oily influent. Finally, they found that the solvent treatment for impurities removal could impair the oleophilicity/ hydrophobicity of the kapok fibers which was crucial for the oily water separation and filtration.

Abdullah et al. (2010) studied in a batch system, the effect of packing density, the oil types and solvent treatment on the sorption characteristics of kapok; a natural sorbent that exhibits excellent hydrophobic-oleophilic characteristics. They evaluated the oil sorption capacity, retention capacity; entrapment stability and kapok reusability. Based on SEM and FTIR analyses, they found that kapok fiber was shown to be a lignocellulosic material with hydrophobic waxy coating over the hollow structures. They supposed that higher packing density at 0.08 g/ml showed lower sorption capacity, but higher percentage of dynamic oil retention, with only 1% of oil drained out from the test cell. In their experiments kapok remained stable after fifteen cycles of reuse with only 30% of sorption capacity reduction, while the oil entrapment stability at 0.08 g/ml packing was high with more than 90% of diesel and used engine oil retained after horizontal shaking. They investigated the effects of chloroform and alkali treatment on the hydrophobic-oleophilic properties and the stability of hollow structures to assess the role of waxy layer on the kapok surface during oil sorption processes. After 8 hr of chloroform and alkali treatment, they observed a 2.1% and 26.3% reduction in sorption capacity, respectively, as compared to the raw kapok. They found that the rigid hollow structure was reduced to flattened-like structure after alkali treatment, though no major structural difference was observed after chloroform treatment. They demonstrated that kapok exhibited stability for prolonged use, with higher saturation time and low bed height reduction at higher packing density and higher oil viscosities. The infrared spectra of chloroform and alkali-treated kapok suggested the wax removal from the kapok surface. Therefore, the removal of wax together with the collapse of rigid, hollow structure could reduce the oil sorption capability though these might increase kapok hydrophilicity. Finally they concluded that the Malaysian kapok has shown great potential as effective lignocellulosic natural oil sorbent, owing to high sorption and retention capacity, structural stability and high reusability.

Deschamps et al. (2003) studied the oil sorption, in aqueous medium by treated cotton and compare its performance with those of hydrophilic or raw cotton. Its reusability was also assessed in their experiments. They used vegetable oil, mineral oil, fuel and petroleum as oil samples in their tests in order to counter the sorption efficiency of the used sorbents. Results of their experiments showed that raw cotton’s sorption capacities were higher than those of treated cotton. They suggested that high affinity could be explained by the presence of waxes on raw cotton fiber surface (around 0.4-0.8%). They found that the saturation speed was lower for raw cotton as contrary to treated cotton, the capillary action was not as important for raw cotton (because of the hydrophilic character of its matrix), and it might play a key role on the sorbent saturation speed, which implied an advantage in using treated cotton. Their research showed that **c**otton could be reused through numerous cycles. They estimated that for different pollutants, raw cotton was more efficient than treated cotton after several cycles and finally they conserved their selective affinity for pollutants.

Li et al. (2012) introduced two methods to develop the oleophilic/ hydrophobic properties of polyurethane foams. Firstly, they modified them by grafting with oleophilic monomer Lauryl methacrylate (LMA) in solvent and secondly they coated LMA microspheres on the surface of the polyurethane foams. They used diesel and kerosene samples for their experiments and pure water/ oil phase and water-oil system were investigated and compared in details. They developed a method for measurement of oil and water sorption capacity of the sorbent (polyurethane foam) that was based on ASTM 726-99 Standard Test Method for Sorbent Performance of Adsorbents. In their research the oil sorption of modified polyurethane foams cubes was enhanced especially in the water-oil system, meeting the challenge for the environmental protection of the marine aquatic ecosystem and their experimental results were promising efficient oil adsorbents.

CHAPTER 6
Multi criteria analysis for the selection of oil adsorbents obtained from modified lignocellulosic or commercial adsorbents

6.1 Introduction

An effective adsorbent is characterized by several criteria. It avoids the need for reducing the size of biomass particles, preserves the pentose (hemicellulose) fractions, limits the formation of degradation products that inhibit growth of fermentative micro organism, minimizes energy demands and limits cost (National Research Council, 1999). The lignocellulosic materials are a significant source of fermentable sugars for industrial use. Pretreatment is the first step towards efficient conversion of lignocelluloses residues to commercial added-value products and remains one of the main barriers preventing technical and commercial success of cellulosic industrial technology. The purpose of any pretreatment of biomass technology is to eliminate or reduce the barriers that exist in order to improve the rate of enzyme hydrolysis and increase the yield of fermentable sugars from cellulose and hemicelluloses (Sidiras and Koukios, 1989).

Pretreatment results must be balanced against their impact on the cost of the downstream processing steps and the trade-off between operating costs, capital costs, and biomass costs (Mosier et al., 2005a). Various pretreatments by acid or alkali, including dilute acid, controlled pH, ammonia explosion, and lime have been applied to prepare cellulosic biomass for subsequent biological conversion (Lee et al., 2009).

Thus, an optimal solution that would be environmentally, technologically, socially and economically feasible is investigated in this chapter by focusing on the selection of oil adsorbents obtained from modified lignocellulosic or commercial adsorbent by Multi Criteria Analysis (MCA). Usually, to implement quantitative information mathematical and statistical analysis methods are applied. Yet, when qualitative information is vital to decision-making, other analysis methods are employed such as MCA in order to help the decision-maker. Despite criticism for lacking of transparent scientific background and subjectivity (Triantaphyllou et al., 1998; Stagl, 2004), MCA enjoys extended applicability and recognition as ‘helping hand’, especially in the domain of environmental management (Wei and Weber, 1996; Hokkanen and Salminen, 1997).

6.1.1 MCA technique

MCA techniques have widespread been used in managerial decisions of several sectors either solely or in combination with other analytical methods (cost-benefit analysis, financial analysis, statistical methods and analyses). Indicative uses of MCA in several scientific domains are environmental management, where MCA techniques are applied for helping the decision-making on policy formation, resource management, emission reduction etc. (Mackay and Robinson, 2000; Salminen et al., 1998; Ferrarini et al., 2001; Georgopoulou et al., 2003). Purpose of any MCA is to contribute to the creation of a decisional background at which insights from as many as possible viewpoints are incorporated. Actually, the MCA is a procedure that helps the decision maker(s) to arrive at a preference ranking (first-best, second-best etc.) among the alternative solutions for a given problem.

6.1.2 Delphi method

The objective of most Delphi applications is the reliable and creative exploration of ideas for the production of suitable information for decision-making. The Delphi method is based on a structured process for collecting and distilling knowledge from a group of experts by means of a series of questionnaires interspersed with controlled opinion feedback (Adler and Ziglio, 1996). This technique allows experts to deal systematically with a complex problem or task. The ‘core’ of the technique is straightforward. It comprises a series of questionnaires sent to a pre-determined group of experts. The questionnaires are constructed so as to elicit responses to the problems posed and to enable the experts advance their views as the work progresses in accordance with the assigned task (Adler and Ziglio, 1996; Rowe and Wright, 1999). The following key characteristics of the Delphi method help the participants to focus on the issues at hand and separate Delphi from other methodologies: anonymity of the participants; structuring of information flow; regular feedback and the role of the facilitator (Rowe and Wright, 1999).

6.1.3 Promethee method

PROMETHEE (Preference Ranking Organization METHod for Enrichment Evaluation), (Brans and Vincke, 1985; Brans et al., 1986), is used as an outranking method, allowing for incomparability ($a\mathrm{R}b$) and weak preference ($a\mathrm{Q}b$) between the alternatives a, b, in addition to the strict preference ($a\mathrm{P}b$) and indifference ($a\mathrm{I}b$) that the ‘classical’ methods are based on. Rather than pointing out a "right" decision, the Promethee method helps decision makers find the alternative that best suits their goal and their understanding of the problem. It provides a comprehensive and rational framework for structuring a decision problem, identifying and quantifying its conflicts and synergies, clusters of actions, and highlights the main alternatives and the structured reasoning behind. Promethee has successfully been used in many decision making contexts worldwide. A non-exhaustive list of scientific publications about extensions, applications and discussions related to the Promethee method was published in 2010, (Behzadian et al.).

6.2 Methodology

Regarding this study, five alternatives are assessed against nine evaluation criteria. An MCA technique was used to rank the alternatives in order of preference. A short description of the study’s methodology follows. Numerical Models are constituted of representative data, set in certain order to reveal a structure and give the necessary information. The choice of a decision proposal among alternatives is an optimization problem; for the solution of this problem, we need a method to select / order / process data / information; the ordered set of data / information is a numerical model as it represents reality in the same mode a functional model does. If an optimization method is not applied, the numerical model cannot obtain operational normative characteristics and is not directly usable for decision making as it also happens with its dialectic opposite pole, the functional model. Subsequently, we implement a numerical model for multi-criteria decision making, giving at the same time a pattern for application of a method on a set of ordered data / information that constitute a numerical model, in a broad sense.

Formerly, the choice of an alternative was solely based on a unique criterion: the cost. Nowadays, multi-criteria methods are followed, which consider simultaneously several criteria. The simplest form of this method is the formation of the sum [$S1, S2, \ldots, Sm$], where Sj (j=1, 2, …, m) is the weighted sum of the grades cij assigned to alternative proposition/suggestion $A\,j$, according to criterion fi :

$$S_j = \sum_{i=1}^{n} w_i \cdot c_{ij} \tag{6.1}$$

where wi is the weight of the criterion i $(i = 1, 2, \ldots, n)$ and $\sum_{i=1}^{n} w_i = 1$; the sum of the weights of all criteria, expressed as percentages or fractions of 1, should be equal to 100% or 1, respectively.

The grades are assigned by experts and lie within a predetermined scale (e.g., from 0 to 10, with the maximum at 10, or from 1 to 5, with the maximum at 5). The optimal selection h is the alternative proposition/suggestion with the highest score, i.e., $Sh = \max [S1, S2, \ldots, Sm]$. Likewise, all the alternative propositions/suggestions can be ranked in descending order of preference: $Sh1 > Sh2 > \ldots > Shm$, where $Sh = Sh1$. When q experts are used, each grade c_{ij} is given as the mean value and the respective standard deviation is calculated. Therefore, instead of the weighted sum, the double weighted sum $wi \cdot cij/eij$ can be used, where eij is the standard deviation that corresponds to the mean cij. This variation of the method is used to reduce the effect of a low-reliability grade (the greater the scattering of the grades c_{ij} assigned by the q experts to an alternative proposition/suggestion Aj, according to criterion fi, the larger the value of the standard deviation, and thus the lower the reliability). Double weighting presumes that standard deviations are not in the vicinity of zero; otherwise some double weighted grades may increase excessively, leading to biased estimates (Batzias, 2005).

In this work eq. (6.1) can be written as

$$S_j = \sum_{i=1}^{9} w_i \cdot c_{ij} \tag{6.2}$$

where j=1, 2, …, 5 and the grades are assigned by the author and lie from 0 to 5, with the maximum at 5.

6.3 Alternatives - evaluation criteria

This work deals with multi criteria choice of adsorbents materials (for oil, dyes, etc.) from modified lignocellulosic biomass and commercial adsorbents. The alternatives examined are:

1. Autohydrolyzed wheat straw, A_1;
2. Sulphuric acid-hydrolyzed wheat straw, A_2;
3. Sodium hydroxide treated wheat straw, A_3;
4. Organosolv treated wheat straw, A_4;

5. Polypropylene oil adsorbent pads, A_5.

The selection and formation of the evaluation criteria was based primarily on: the estimated costs and benefits accruing from applying the alternatives, the extent to which each method contributes to environmental protection, thus implying the method's sustainability, the specific technological features, market penetration potential and reliability of each method, and the feedstock potential and the characteristics of any other material that possibly could be utilised in applying each alternative.

An optimal pretreatment should fulfil as many as possible of the following requirements : (a) simple and economic operation; (b) particle size reduction, if necessary, should be achieved at low cost; (c) reduced consumption of energy, water and chemicals; (d) limited corrosion effects; (e) ability for reaching favourable effects on the lignocellulosic material structure; (f) reduced polysaccharide losses; (g) recovery of valuable products from hemicelluloses; (h) limited generation of unwanted products from polysaccharides (for example, dehydration products such as furfural or 5-hydroxymethylfurfural) or lignin; (i) production of pretreated solids with enhanced cellulose contents and high susceptibility toward enzymatic hydrolysis; (j) recovery of high-quality lignin or lignin-derived compounds; and (k) limited waste generation (Romani et al., 2012).

The evaluation criteria against which the alternatives assessed were the following:

- capital cost (from depreciation through retention time), f_1;
- operating cost (including energy and raw material price), f_2;
- health occupational (including safety), f_3;
- reliability, f_4;
- environmental friendliness (through Life Cycle Assessment), f_5;
- adsorption efficiency (e.g. with Methylene Blue), f_6;
- widely spread (available) know-how, (maturity of technology), f_7;
- contribution to sustainability at local level (including the Industrial Ecology aspect), f_8;
- marketability within a wider network (depended mainly on ageing), f_9.

6.3.1 Autohydrolyzed wheat straw

Autohydrolysis, (also called hot water processing, steam explosion or hydrothermal pretreatment), is one of the biomass fractionation processes, is carried out by heating an aqueous suspension of the lignocellulosic materials, and results in the partial hydrolysis of hemicellulose into soluble fragments (Balat et al., 2008). This pretreatment combines mechanical forces and chemical effects due to the autohydrolysis of acetyl groups present in hemicellulose (Alvira et al., 2010). Autohydrolysis covers a wide range of treatments, including and processes based on water, steam explosion, aqueous separation, and hot-water systems. Commercial products of biomass fractionation include levulinic acid, xylitol, and alcohols. Operating under suitable conditions, hemicelluloses can be extensively converted into soluble saccharides (Garrote et al., 1999), whereas the treated solids show an increased susceptibility to cellulolytic enzymes (Wyman et al., 2005), enabling their utilization as substrates for bio-ethanol production.

Autohydrolysis is a process well documented tested at several levels and at various institutions and satisfies all the requirements of the pretreatment process (Taherzadeh and Karimi, 2007). According to McMillan, (1994), it is the most commonly used method for pretreatment of different lignocellulosic materials (Table 6.1).

Table 6.1 Autohydrolyzed materials according to references

Material	Reference
Olive-tree-pruning biomass	Cara et al., (2007)
Poplar biomass	Negro et al., (2003)
Mixed hardwood chips	Schultz et al., (1984)
Rice hulls	Schultz et al., (1984)
Corn stalks	Schultz et al., (1984)
Sugarcane bagasse	Schultz et al., (1984)
Sunflower stalks	Ruiz et al., (2008)
Corn stover	Mosier et al., (2005b)
Wheat straw	Viola et al., (2008)
Barley straw	Viola et al., (2008)
Oat straw	Viola et al., (2008)

Cara et al., (2007), studied pretreatment of olive-tree-pruning biomass, by either liquid hot water or steam explosion, which was used as a substrate for enzymatic hydrolysis. Negro et al., (2003), evaluated steam explosion to enhance ethanol production from poplar biomass. Schultz et al., (1984), compared effectiveness of steam explosion pretreatment on mixed hardwood chips, rice hulls, corn stalks, and sugarcane bagasse. Liquid hot water has also been used as a pretreatment method for agricultural residues like sunflower stalks (Ruiz et al., 2008) and corn stover (Mosier et al., 2005b). Viola et al., (2008), reported steam-explosion treatment of wheat, barley, and oat straws. This treatment is already used as first step in the fermentable sugars for bio-ethanol production industry (Lee et al., 2009; Nabarlatz et al., 2007).

Autohydrolysis is recognized as one of the most cost-effective pretreatment processes for hard woods and agricultural residues, but it is less effective for softwoods (Sun and Cheng, 2002). It is considered the most cost-effective option for hard wood and agriculture residues (Vessia, 2005). The pretreatment expenses can be covered by the produced fermentable sugars for the bio-ethanol production industry, which is subsidised in the EU Countries (Sidiras et al., 2011a). Its energy costs are relatively moderate and the general process has been demonstrated on a commercial scale at the Masonite plants (Chum et al., 1985). The absence of acid reduces both capital and operational costs, reduces environmental impact and indicates the economical advantages of aqueous-based processes compared to other hydrolytic technologies (Carvalheiro et al., 2008). As regards the environmental friendliness of this process through Life Cycle Assessment, the total Green House Gas (GHG) emissions, (kg equivalent CO_2), were -237.70 and -555.40 for hot water pretreatment and for steam explosion pretreatment, respectively (Kumar and Murthy, 2012).

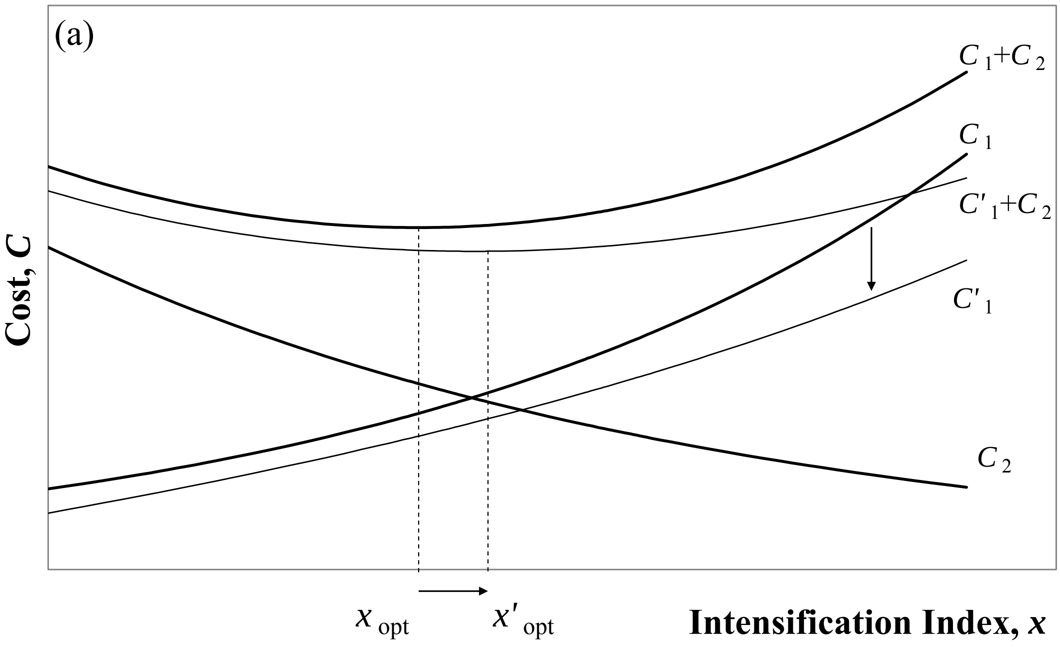
Autohydrolysis comparing to other pretreatment methods has the advantage that is using pure and easily recyclable water as a reagent. The exclusive use of water is cost- and quality effective (Sidiras et al., 2011a). It’s a chemically free process as no chemicals (acids, salts, based organic solvents) are needed; simple and environmental friendly (Raspolli-Galletti and Antonetti, 2011; Romaní et al., 2010). Water, itself, acts as an acid at high temperatures (Weil et al., 1997). It is very clear that autohydrolysis is a more environmentally sound method and has processing advantages over acid pretreatments (Lee et al., 2009).

The advantages of autohydrolysis pretreatment include the low energy requirement compared to other methods and no recycling or environmental costs. Thermal energy demand can be covered by using cylindrical parabolic concentrators of solar radiation which is adequate for this purpose, even in the Central-Northern

European Countries (Sidiras et al., 2011a). The temperature required in the reactor is up to 240°C, which means that we need a temperature level of about 290°C at the collector solid/liquid interface, assuming 15% thermal loss, estimated for ambient temperature in islands of South Aegean Sea. The IST PT-2 solar parabolic-trough collector (Fernandez-Garcia et al., 2010) has been chosen for this purpose, having the following characteristics: operating temperature, 288°C; working fluid, pressurized water; aperture area, 14 m^2; aperture width, 2.3 m; length, 6.1 m; focal length, 0.8 m; absorber tube diameter, 51 mm; cover tube diameter, 75 mm; rim angle, 72°; acceptance angle, 2.4°; geometric concentration ratio, 14.36; peak optical efficiency, 0.76; reflectance, 0.89; absorptance, 0.97; emittance, 0.2.

Consequently, the investment for the biomass processing installation can be subsidized because of its contribution to adsorption materials saving and solar energy utilization in a cost-effective mode, influencing the optimal process intensification index x-value, as shown subsequently. The optimal x-value can be estimated at minimum cost $C_{min}=(C_1+C_2)_{min}$, where C_1 is the energy cost and C_2 is the adsorption materials cost. The former is an increasing function of x with decreasing rate (i.e., $dC_1/dx>0$, $d^2C_1/dx^2<0$), because of the validity of the Law of Diminishing Returns (LDR), holding *a fortiori* in energetics, since both capital and operating (including losses) cost increase disproportionately with temperature. C_2 is a decreasing function of x for $T < 200^{o}C$, with increasing algebraic or decreasing absolute rate (i.e., $dC_2/dx<0$, $d^2C_2/dx^2>0$ or $d|dC_2/dx|/dx<0$), since higher intensification implies the use of lesser treated biomass quantity (but of improved quality) substituted for the adsorptive material previously required, thus leading to more saving of consumables, although such a saving obeys also to the LDR. Consequenlty, x_{opt} is depermined as the abscissa of the equilibrium point (in the tradeoff between the conflict partial costs) at C_{min} or $MC_1=MC_2$, where $MC_1=dC_1/dx$ and $MC_2=|dC_2/dx|$, are the marginal costs of C_1 and C_2, respectively.

When using a locally available low-cost energy source, as it is the case of solar energy utilization in a remote island in the Mediterranean Sea (as quoted above), where electricity is rather expensive, the C_1-curve moves downwards becoming also more flat, since energy cost saving is more expressed in the region of high x-values; as a result, x_{opt} is shifting top x'_{opt}, where $x'_{opt}>x_{opt}$ (Fig. 6.1a). When the investment is subsidized, the C_2-curve is also moving downwards becoming steeper, since financial support is more effective in the region of high x-values, where there are greater margins for improvement (these margins are narrower in the low *x*-values, due to the LDR); as a result, x_{opt} is shifting to x''_{opt}, where $x''_{opt} > x_{opt}$ (Fig. 6.1b). Evidently, total shifting is determined by adding the two vectors (x'_{opt} - x_{opt}) and (x''_{opt} - x_{opt}), which have the same direction.



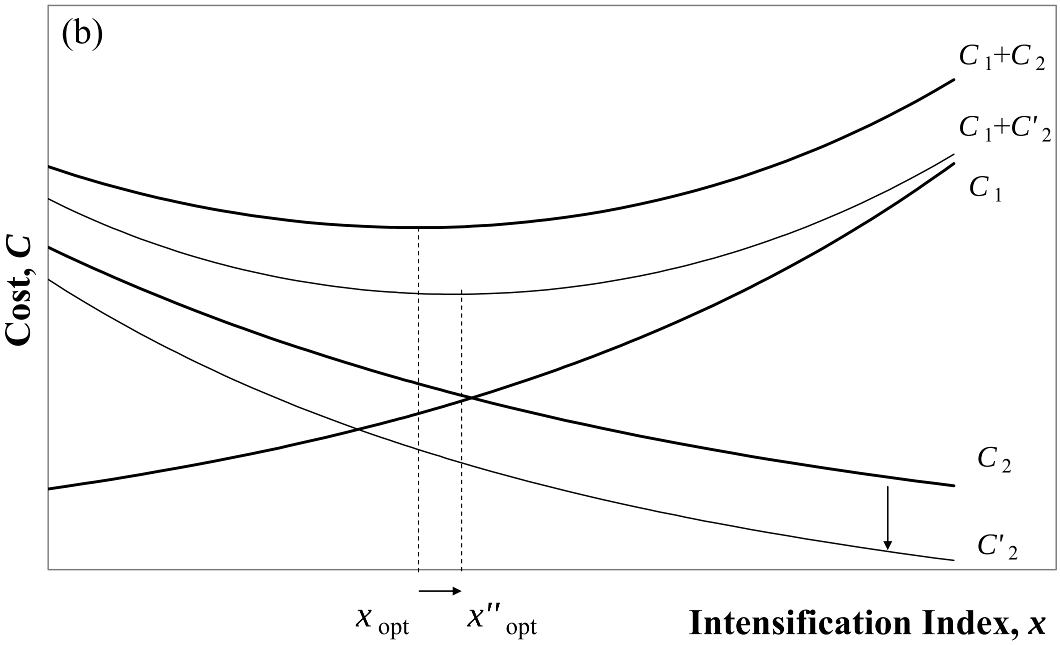


Fig. 6.1 Shifting of process intensification optimal value x_{opt}, when (a) solar thermal energy (instead of electrical or conventional thermic form fossil fuels) is utilised, and (b) capital cost decreases due to governmental subsidy of the investment for the biomass treatment installation

It also causes hemicellulose degradation and lignin transformation (Kumar et al., 2009); increases the accessible surface area, shows higher substrate digestibility, de-polymerize the lignin and solubilize the hemicellulose (Raspolli-Galletti and Antonetti, 2011). Autohydrolysis process offers several attractive features when compared to other pretreatment technologies, including the potential for significantly lower environmental impact, lower capital investment, and more potential for energy efficiency, less hazardous process chemicals and conditions and complete sugar recovery (Avellar and Glasser, 1998). Among the main advantages, it is worth to mention the possibility of using high chip size as energy use for obtaining small chips size before pretreatment can make up one third of the power requirements of the entire process (Hamelinck et al., 2005).

Furthermore, as wheat straw is an industrial waste and no addition of chemicals is required, we argue that this process of adsorbent modification may be considered to take place within an 'Industrial Ecology' framework, since a (solid) waste is used to treat another (aquatic) waste, contributing to pollution abatement without entailing excessive cost. This is an argument *a fortiori*, when additives (e.g., chloride salts) are used to enhance adsorptivity on condition they are available in the vicinity as waste or low value by-products of proper quality (Sidiras et al., 2011a). Diesel oil and crude oil adsorbency values of autohydrolyzed wheat straw were 7.83 and 7.28 (g/g), respectively, in the case of pure liquids (measured in this study). Diesel oil and crude oil adsorbency values of autohydrolyzed wheat straw were 6.13, 8.36 and 6.65, 6.91 (g/g), respectively, in the case of oil spills on freshwater and seawater (measured in this study). From the other hand, autohydrolysis destructs a portion of the xylan fraction, leads to incomplete disruption of the lignin-carbohydrate matrix and causes generation of compounds inhibitory to micro-organisms (Kumar et al., 2009). Sometimes needs a combination with other treatments and causes formation of inhibitors (Raspolli-Galletti and Antonetti, 2011).

Chum et al., (1985), compared autohydrolysis, organosolv and wet oxidation pretreatments of lignocellulosic biomass for its conversion to alcohol fuels. They prepared, from the available data, for each of these processes, heat balances, material balances, and economic summaries. The cost of production was determined both in cents per pound of cellulose produced and in dollars per gallon contributed to the cost of ethanol. They analyzed the effects of variations in such important process parameters as feedstock cost, steam cost, solvent cost, and recovery efficiency. They found that steam explosion pretreatment has had a significant amount of development. They concluded this process is the most economical, both in terms of the cellulose pulp produced and its contribution to the ethanol production cost. All costs were based on third quarter 1982 dollars. The total equipment cost for each process was multiplied by 2.7 to yield the installed cost for the portion of the plant inside battery limits (ISBL). This factor covered installation, piping, engineering, construction overhead, contingencies, contractors' fees, and special charges. The cost of equipment outside battery limits (OSBL) or off site was estimated at 30% of ISBL costs and included capital for the boiler (plus the fuel storage and handling system), steam and water distribution, buildings, site development, utilities, and pollution control. The total represents the total fixed investment (TFI) allocated to pretreatment as part of a cellulose-to-ethanol plant. Working capital requirements were specified as four months' production costs less depreciation. Capital and operating costs for the steam explosion pretreatment, (by-product combustion option), of lignocellulosic biomass for its conversion to alcohol fuels were estimated by Chum et al., (1985). Capacity was 700,000 tn wood chips including 300,000 tn/yr cellulose and operating was 8,000 hr/yr for 143.85 million L/yr ethanol. For the year 1982, the capital cost (including battery limits and off sites) reached at 29.84 million $ of year 1982. Annual operating cost for raw materials (wood chips-feedstock) reached at 21 million $ and for utilities (including power, cooling water, steam, operating costs and expenses) reached at 5.53 million $ of year 1982. In terms of year 2014, the capital cost reaches at 54.02 million € while the annual operating cost reaches at 38.02 million $ for raw materials and at 10.01 million $ for utilities.

We can produce instead of 143.85 million L/yr of ethanol 700,000 tn/yr wood chips X 50% = 350,000 tn/yr of adsorbate. So, for the same input capacity we can produce adsorbate with 50% x 54.02 million € = 27.01 million € capital cost and 100% x 38.02 million € = 38.02 million € operating cost for raw materials and 50% x 10.01 million € = 5 million € operating cost for utilities. To estimate the annualized product price we take into account taxes, insurance, depreciation, interest and return on investment equal to 33.33% according to Chum et al., (1985). It can be estimated that the adsorbate can be sold at the price of [(38.02+5)x1.33]x1,000,000 €/350,000 tn=164 €/tn =0.164 €/kg. It is suggested the co-production of ethanol and adsorbate or other materials according to the bio-refinery frame.

The cost of wheat straw biomass production is 0.03 €/kg (Manitoba Agriculture, Food and Rural Development, 2014) while the wood chips cost was 0.05 €/kg according to Chum et al., (1985). The annual production of wheat straw in Greece 2000 was 1114 thousand tons, according to official data from the Ministry of Agricultural. In the case of pure liquids the one month ageing of the autohydrolyzed wheat straw was 2.40% and 11.70% for the cases of diesel and crude oil, respectively; while in the case of oil spills on freshwater the one month ageing was 7.00% and 8.50% for the cases of diesel oil spill and crude oil spill, respectively (measured in this study). The same about results were for the case of the one year ageing of the adsorption material.

6.3.2 Sulfuric acid-hydrolyzed wheat straw

The main objective of the dilute acid pretreatment is to solubilize the hemicellulosic fraction of the biomass and to make the cellulose more accessible to enzymes (Alvira et al., 2010). Dilute acid pre-treatment at moderate temperatures using mainly sulfuric acid was used for converting lignocellulosic biomass, including the hemicellulose fraction, to soluble sugars, followed by enzymecatalyzed hydrolysis of the cellulosic fraction to glucose (Balat et al., 2008). In these conditions, the beta-glycosidic linkages of the cellulose molecular chains are cleaved by adding water, and thus formed fractions with shorter chains, but with identical basic structure. During the acid hydrolysis of cellulose, monosaccharides that match glucan and xylan formed largely and mannan, galactan and arabinan in a small percentage, depending on the type of cellulosic material. For understanding the mechanism of the hydrolysis, it is necessary to study the hydrolysis of each component separately (Wenzl, 1970). In acid hydrolysis we can fractionate (Koukios, 1989) the three basic components of lignocellulosic: hemicelluloses, cellulose and lignin.

Dilute acid pretreatment is the technology that has been claimed to be closest to commercialization (Holtzapple et al., 1989). Dilute H_2SO_4 has been used to commercially manufacture furfural from cellulosic materials (Root et al., 1959; Zeitsch, 2000). The pretreatment has been tested extensively for a large number of different lignocellulosic feed-stocks, has been scaled-up and operated at the pilot-plant scale at the Iogen demonstration plant in Canada (Jorgensen et al., 2007).

In the dilute-acid process, the reaction is carried out at high temperature and pressure, and because of low yields of glucose from cellulose in the hydrolysis step, the ethanol yield is low (Kumar et al., 2009). In particular, the high capital cost for high–pressure equipment may represent an obstacle to the commercialization of this lignocellulosic pretreatment (Luterbacher et al., 2010). Although dilute-acid pretreatment can significantly improve cellulose hydrolysis, its cost is usually higher than those of physicochemical pretreatment processes such as autohydrolysis (Kumar et al., 2009). Furthermore, acid pretreatment results in costly materials of construction, high pressures, neutralization and conditioning of hydrolysate prior to biological steps, slow cellulose digestion by enzymes, and non productive binding of enzymes to lignin (Hsu et al., 1980). This process is not sufficiently effective for commercial development unless the feedstock is very cheap (Jeffries and Jin, 2000). In 2009 there was low cost of feedstock (0.05-0.06 €/kg; 3-4 €/GJ) e.g. straw, wood residues, energy crops (Wild et al., 2009). In terms of year 2014, cost of feedstock is 0.06-0.07 €/kg; 3.33-4.44 €/GJ. The price for 98% purity of sulfuric acid is 0.18-0.37 €/kg (ICIS).

The dilute sulfuric acid pretreatment can achieve high reaction rates, significantly improves cellulose hydrolysis, hydrolyzes hemicellulose to xylose and other sugars and alters the lignin structure (Esteghlalian et al., 1997). Advantages of this process include increased substrate digestibility and hemicellulose solubilisation (Raspolli-Galletti and Antonetti, 2011). Dilute H_2SO_4 is a strong catalyst that highly improves the hemicellulose removal (Balat et al., 2008). Diesel oil and crude oil adsorbency values of sulfuric acid-hydrolyzed wheat straw were 5.24 and 5.38 (g/g), respectively, in the case of pure liquids (measured in this study). As regards the environmental friendliness of this process through Life Cycle Assessment, the total Green House Gas (GHG) emissions (kg equivalent CO_2) was -235.60 for the dilute acid pretreatment (Kumar and Murthy, 2012).

On the other hand, the addition of the acid causes many drawbacks related to equipment corrosion leading to greater cost, higher amounts of degradation products and the necessary step of acid recovery - neutralization with consequent formation of wastes (Raspolli-Galletti and Antonetti, 2011). It has been shown that materials that have been subjected to acid hydrolysis can be harder to ferment because of the presence of toxic substances (Galbe and Zacchi, 2007; Kumar et al., 2009). Acid hydrolysis requires high temperature and low pH which results in corrosive conditions; does not achieve high yield ethanol; forms several inhibitory compounds (Taherzadeh and Karimi, 2007). Furthermore, dilute acid pretreatment results in costly materials of construction, high pressures, neutralization and conditioning of hydrolyzate prior to biological steps, slow cellulose digestion by enzymes, and non productive binding of enzymes to lignin (Wyman et al., 2005).

Humbird et al., (2011), estimated the capital and the operating cost of the dilute-acid pretreatment for the biochemical conversion of lignocellulosic biomass (corn stover) to ethanol. The conceptual design they presented reported ethanol production economics as determined by 2012 conversion targets and “n^{th}-plant” project costs and financing. For the bio-refinery they described, processing 772,676 tn/yr corn stover at 76% theoretical ethanol yield 300 L/tn, i.e. 231.8 million L/yr of ethanol, with an expected 8,410 operating hours per year (96% up-time), the ethanol selling price was 0.42 €/L in 2007 prices. The capital cost of the installed equipment including pretreatment, neutralization/ conditioning, boiler/ turbo generator and utilities reached at 105,800,000 $, i.e. 46% of the total capital cost of the installed equipment which was 232,000,000 $. The capital cost of the added direct and indirect costs reached at 86,563,000 $. The total capital investment was 192,364,000 $. Annual operating cost for feedstock and handling was 45,200,000 $ and for sulfuric acid, other raw materials, waste disposal and other fixed costs reached at 21,600,000 $. The capital depreciation was 13,400,000 $, the average income tax was 7,500,000 $ and the average return on investment was 34,600,000 $. In terms of year 2014, the total capital investment was 162,162,852 €. Annual operating cost for feedstock and handling was 38,103,600 € and for sulfuric acid, other raw materials, waste disposal and other fixed costs reached at 18,208,800 €. The capital depreciation was 11,296,200 €, the average income tax was 6,322,500 € and the average return on investment was 29,167,800 €.

We can produce instead of 231.8 million L/yr of ethanol 772,676 tn/yr corn stover X 50% = 386,300 tn/yr of adsorbate. So, for the same input capacity we can produce adsorbate with 50% x 162,162,852 € = 81,081,426 € capital cost, 100% x 38,103,600 € = 38,103,600 € operating cost for feedstock and handling and 100% x 18,208,800 € = 18,208,800 € operating cost for sulfuric acid, other raw materials, waste disposal and other fixed costs. It can be estimated that the adsorbate can be sold at the price of [(81,081,426 € /10 yr) + 38,103,600 € + 18,208,800 €]/ 386,300 tn/yr =167 €/tn=0.167 €/kg. The ethanol selling price is 0.49 €/L. For the same ethanol production capacity with the above mentioned autohydrolysis method the capital cost can be estimated as follows and reaches at: 0.62 x 81,000,000 € = 50,220,000 €, while the operating cost reaches at 0.62 x 56,312,400 = 34,913,688 €. It is suggested the co-production of ethanol and adsorbate or other materials according to the bio-refinery frame.

6.3.3 Sodium hydroxide treated wheat straw

Some bases can be used for the pretreatment of lignocellulosic materials, and the effect of alkaline pretreatment depends on the lignin content of the materials (McMillan, 1994; Fan et al., 1987). Sodium, potassium, calcium, and ammonium hydroxides are suitable alkaline pretreatment agents. Of these four, sodium hydroxide has been studied the most (Fox et al., 1989; Elshafei et al., 1991; Soto et al., 1994). Most of these chemicals specifically target hemicellulose acetyl groups and lignin-carbohydrate ester linkages. These reactions help solubilise and extract lignin from the biomass, reducing non-specific binding during enzymatic hydrolysis (Kim and Lee, 2005). The characteristic of alkaline pre-treatment is that it can remove the lignin without having big effects on other components (McMillan, 1997). Alkali pre-treatment reduces the lignin and hemicellulose content in biomass, increases the surface area, allowing penetration of water molecules to the inner layers, and breaks the bonds between hemicellulose and lignin carbohydrate. This pretreatment process can be performed at room temperature and times ranging from seconds to days (Alvira et al., 2010). Dilute NaOH is usually used for alkali pre-treatment (Lee, 2005; Balat et al., 2008).

Dilute NaOH treatment of lignocellulosic materials has been found to cause swelling, leading to an increase in internal surface area, a decrease in the degree of polymerization, a decrease in crystallinity, separation of structural linkages between lignin and carbohydrates, and disruption of the lignin structure (Fan et al., 1987). The digestibility of NaOH-treated hardwood was reported to increase from 14% to 55% with a decrease of lignin content from 24-55% to 20%. However, no effect of dilute NaOH pretreatment was observed for softwoods with lignin content greater than 26% (Millet et al., 1976). Dilute NaOH pretreatment was also found to be effective for the enzymatic hydrolysis of straws with relatively low lignin contents of 10-18% (Bjerre et al., 1996). Chosdu et al., 1993, used a combination of irradiation and 2% NaOH for pretreatment of corn stalk, cassava bark, and peanut husk. Alkali pretreatment processes utilize lower temperatures and pressures than other pretreatment technologies (Mosier et al., 2005a; Carvalheiro et al., 2008). It’s usually more effective on hardwood, herbaceous crops and agricultural residues with low lignin content than on softwood with high lignin content (Sills and Gossett, 2011). Using alkaline chemicals to remove lignin has been known to improve cellulose digestibility for years, but sodium hydroxide and other bases are too expensive and too difficult to recover and recycle to make them viable for producing fuels and chemicals (Hsu, 1996). Considering economic and environmental aspects, dilute NaOH treatment would be much more suitable than the concentrated NaOH pre-treatment (Balat et al., 2008). Acid based pretreatment processes have been shown to be effective on a wide range of lignocellulose substrate, but are relatively expensive (Mosier et al., 2005a).

The advantages of this pretreatment include the removing of hemicelluloses and lignin and the increasing of the accessible surface area (Kumar et al., 2009). Furthermore, this method contributes to the hemicellulose and lignin hydrolysis, requires mild conditions and increases the substrate digestibility (Raspolli-Galletti and Antonetti, 2011). Alkali pretreatments are more effective for lignin solubilization, exhibiting minor cellulose and hemicellulose solubilization than acid or hydrothermal processes (Carvalheiro et al., 2008). Also, in comparison with acid processes, alkaline ones cause less sugar degradation and many of the caustic salts can be recovered and/or regenerated (Raspolli-Galletti and Antonetti, 2011).

Oil adsorbency values of sodium hydroxide treated straw were, for both, 0.58 (g/g), in the case of oil spills on water (Ibrahim et al., 2009; 2010). As regards the environmental friendliness of this process through Life Cycle Assessment, the total Green House Gas (GHG) emissions (kg equivalent CO_2) was -131.00 for the dilute alkali pretreatment (Kumar and Murthy, 2012).

On the other hand, alkali process requires long residence times and forms irrecoverable salts that are incorporated into biomass (Kumar et al., 2009), making the treatment of a large amount of salts a challenging issue for alkaline approach. Furthermore, if performed at room temperature, high concentrations of base are required; alkaline reagents can also remove acetyl and various acid substitutions on hemicellulose, thus reducing the accessibility of hemicellulose and cellulose to enzymes (Raspolli-Galletti and Antonetti, 2011). Price for 99% purity of sodium hydroxide is 0.33 €/kg (ICIS). The capital and the operating cost of this method are assumed to be approximately the same with the above presented sulfuric acid-hydrolysis method slightly modified taking into account the data of Table 6.3 about fixed capital cost and Table 6.4 on energy requirements .

6.3.4 Organosolv treated wheat straw

Organosolv may be used to provide treated cellulose suitable for enzyme hydrolysis, using solvents to remove lignin (Itoh et al., 2003; Pan et al., 2006). The organosolv method is a promising pretreatment strategy, and it has attracted much attention and demonstrated the potential for utilization in lignocellulosic pretreatment (Botello et al., 1999). In the organosolvation process, an organic or aqueous organic solvent mixture with inorganic acid catalysts (HCl or H_2SO_4) is used to break the internal lignin and hemicellulose bonds. The mixture is heated to dissolve the lignin and some of the hemicellulose and leave a reactive cellulose cake. In addition, a catalyst is sometimes added either to reduce the operating temperature or to enhance the delignification process. Most of these processes produce similar results and for that reason are grouped as a single class (Chum et al., 1985).

The solvents commonly used in the process are methanol, ethanol, acetone, ethylene glycol, triethylene glycol, and tetrahydrofurfuryl alcohol (Chum et al., 1988). For economic reasons aqueous ethanol is generally the preferred solvent, having low boiling point, toxicity and cost, but the pretreatment process is always conducted under high pressure with increase of the equipment cost (Raspolli-Galletti and Antonetti, 2011). Organic acids such as oxalic, acetylsalicylic, and salicylic acids can also be used as catalysts in the organosolvation process (Sarkanen, 1980). In essence, the organosolv process involves simultaneous pre-hydrolysis; delignification of lignocellulosic biomass supported by organic solvents and, usually, dilutes aqueous acid solutions. A high yield of xylose can usually be obtained with the addition of acid.

Liquid-to-solid ratio (LSR) used in this pretreatment should be optimized. Low LSR reduces the amounts of water and solvent in the system, with reduction of capital costs (smaller tanks and pumps are required for the same quantities of feedstock). Operating costs (especially energy for pumping and solvent recovery) are also reduced when low LSR is selected. From the other hand, separation equipment, especially filters and centrifuges, must work more efficiently since inlet and outlet solid concentrations are much higher. Also, at a very low LSR (below 4:1) re-precipitation of dissolved lignin onto the cellulose fiber can take place, thus limiting its successive enzymatic hydrolysis (Zhao et al., 2009). Advantages of organosolv pretreatment include efficient hydrolysis and solubilisation of lignin and hemicelluloses (Raspolli-Galletti and Antonetti, 2011). Comparing to other chemical pretreatments the main advantage of organosolv process is the recovery of relatively pure lignin as a by-product (Zhao et al., 2009). Solvents generally used in the organosolvation process need to be drained from the reactor, evaporated, condensed, and recycled to reduce the high cost (Kumar et al., 2009). Removal of solvents from the process system is necessary using appropriate extraction and separation techniques, e.g., evaporation and condensation. Solvents need to be separated because they might be inhibitory to enzymatic hydrolysis and fermentative micro organisms (Sun and Cheng, 2002). Organic solvents are often harmful to humans and the environment (She et al., 2009). Another considerable drawback of organosolv pretreatment is the high cost for plant and solvents (Raspolli-Galletti and Antonetti, 2011).

The organosolv pretreatment with 0.045N H_2SO_4 and 50% w/w butanol in liquid phase – 50% w/w water at 180^o C for 0 to 50 min (+50 min preheating time) did not enhanced the adsorptivity of diesel and crude oil for lignocellulosic materials. Adsorbency values were 0.51 (g/g), for both, in the case of oil spills on water. These results derived from older experiments in our lab. The price for 95-99.9% purity of industrial ethanol is 0.29-0.44 €/kg (ICIS).

Capital and operating costs for the organosolv pretreatment, (by-product combustion option), of lignocellulosic biomass for its conversion to alcohol fuels were estimated by Chum et al., (1985). Liquid-to-wood ratio was 4:1 using 70% methanol. Capacity was 694,924 tn wood chips including 300,000 tn/yr cellulose and operating was 8,000 hr/yr for 143.85 million L/yr ethanol. For the year 1982, the capital cost including battery limits and off-sites reached at 32.78 million $. Annual operating cost for raw materials (wood chips-feedstock, sulfuric acid and methanol) reached at 27.80 million $ and for utilities (including power, cooling water, process water, operating costs and expenses) reached at 4.78 million $ of year 1982. In terms of year 2014, the capital cost reaches at 59.33 million € while the annual operating cost reaches 50.32 million € for raw materials and 8.65 million € for utilities.

We can produce instead of 143.85 million L/yr of ethanol 700,000 tn/yr wood chips X 50% = 350,000 tn/yr of adsorbate. So, for the same input capacity we can produce adsorbate with 50% x 59.33 million € = 29.67 million € capital cost and 100% x 50.32 million € = 50.32 million € operating cost for raw materials and 50% x 8.65 million € = 4.33 million € operating cost for utilities. To estimate the annualized product price we take into account taxes, insurance, depreciation, interest and return on investment equal to 37.5% according to Chum et al., (1985).

It can be estimated that the adsorbate can be sold at the price of [(50.32+4.33)x1.375]x1,000,000 €/350,000 tn=214 €/tn =0.214 €/kg. It is suggested the co-production of ethanol and adsorbate or other materials according to the bio-refinery frame.

6.3.5 Polypropylene oil adsorbent pads

The most widely used adsorbents are synthetic sorbents made from high molecular weight polymers, such as polyurethane and polypropylene because of their highly oleophilic and hydrophobic properties advantage (Choi and Cloud, 1992). They are available under various trade names and forms, like polypropylene oil adsorbent pads. Polypropylene oil adsorbent pads porous structure is formed by a system of open pores and polymer bridges. The sizes of the pores are usually 50-200 μm. The surfaces of the polypropylene pads are smooth (Bogdan et al., 2008). Oil adsorbent pads used in this study (manufactured by New Naval Ltd located in Piraeus, Greece) were 100% of polypropylene, thermally bonded, flame resistant, highly durable, floatable and didn't rip, tear or fray even when saturated. Their bright white color makes absorbed oil easier to see; draws attention to machine leaks and clearly shows saturation level during a real spill response incident.

Polypropylene fibers are considered to be efficient adsorbents because of their rapid saturation-adsorption rate, simple recovery method and high selectivity for the oil pollutants over the water. These features make polypropylene fiber very attractive as an adsorbent for the treatment of oil spillage (Li and Wei, 2012a). They have good hydrophobic and oleophilic properties and high sorption capacity (Al-Majed et al., 2012). Polypropylene oil adsorbent pads have the potential to be applied to organics remediation because of their rapid adsorption equilibria and the fact that organics adsorbed onto the polypropylene pads can be recovered through simple squeezing.

Many types of polypropylene adsorbents have been commonly used to remove oil pollutants, and these adsorbents are of considerable importance for rapid cleanup (Li and Wei, 2012b). It has been demonstrated that the oil sorption capacity of these synthetic materials can be increased further by blending them with other natural products, though the blending percentage should be further optimized to obtain the best oil sorption performance (Adebajo et al., 2003).

From the other hand, the non-biodegradability or the very slowly biodegradability of synthetic adsorbents is a major disadvantage (Choi and Cloud, 1992; Deschamps et al., 2003; Sun et al., 2002; Teas et al., 2001), as bio-degradation is an important property for the sorbent in two ways. First of all, it can provide an alternative method for disposal, versus land-filling or incineration, of the oil-soaked sorbent. Landfill disposal is environmentally undesirable and incineration is very expensive (Adebajo et al., 2003). Secondly, because a fraction of the sorbent material is unrecoverable in a large-scale oil-spill cleanup, the biodegradable sorbent is preferred to minimize subsequent environmental problems (Choi, 1996). Furthermore, polypropylene adsorbents are not naturally occurring as mineral products (Teas et al., 2001). Also, the low retention performances of the polypropylene oil adsorbent pads may cause secondary pollution, their application has been limited by their lower adsorption capacities, and their lack of elasticity has dramatically limited their reuse (EI-Hag Ali et al., 2008; Lin et al., 2010). Moreover, the use of polypropylene adsorbents is not always ideal, for example, the low surface free energy of fiber matrix leaded the adsorption capacity of polypropylene fiber for organic chemical to be unsatisfactory, which limited their intended application in organic chemical spill-treatment (Li and Wei, 2012a).

Choi, (1996), studied the polypropylene adsorbents with fiber structure and used the light crude as type of oil. He found that their sorption capacity was 10 x of their weight. Their ability to be reusable and available was significant but from the other hand they weren’t environmental friendly and they were too expensive. Diesel oil and crude oil adsorbency values of polypropylene oil adsorbents pads were 10.26 and 12.21 (g/g), respectively, in the case of pure liquids. Diesel oil and crude oil adsorbency values of polypropylene oil adsorbents pads were 9.02, 9.82 and 9.51 (g/g), respectively, in the case of oil spills on freshwater and seawater (measured in this study).

The price for polypropylene oil absorbent pads (heavy weight, 15" x 19", 100/case, perforated, absorbs 29.1 gal/case, 13 lbs) is 47.99 $. This means, that the price for polypropylene oil absorbent pads (heavy weight, 38.10 x 48.26 cm, l00/case, perforated, absorbs 110.16 kg/case, 5.90 kg), is 35.48 €, i.e. 6.01 €/kg. Their lifetime is three years and the profit margin of the adsorbent industry is about 12% (Universal Adsorbents & Chemicals P.L.C.)

6.4 Weighing the criteria - pair wise comparison

6.4.1 Weighing the criteria

It was taken into account that not all the criteria were of equal significance in the analysis. In order to indicate the particular significance for each of the assessment criteria in the decision-making process, different weights were assigned to each criterion. Weighing the criteria is a more or less subjective procedure for the decision-maker, depending largely on the prevailing (at the time of the study) economic, environmental, institutional, technological and social conditions, and on the decision-makers knowledge and expertise on similar research grounds (Prastakos, 2003).

Table 6.2 Weights attributed to evaluation criteria

Evaluation criteria	Weight coefficient
Capital cost (f_1)	18%
Operating cost (f_2)	13%
Health occupational (f_3)	9%
Reliability (f_4)	11%
Environmental friendliness (f_5)	10%
Adsorption efficiency (f_6)	13%
Widely spread know-how (f_7)	8%
Contribution to sustainability… (f_8)	7%
Marketability within a wider…(f_9)	11%
Sum	100%

Finally, the weights were assigned according the allocation method. This is a method for direct assignment of weights to a set of evaluation criteria. The decision-maker is responsible to allocate a number of weighting units (100) to the criteria, according to the importance they mean to him. To the most important criterion will assign the greatest number of units, to the next important a lower number of units and so on, until the total number of units is equal to 100 (Diakoulaki, 2003) and are shown on Table 6.2.

6.4.2 Pair wise comparison

As regards the first criterion f_1: capital cost, it should be mentioned that although huge information about the effects of different pretreatments on biomass composition and sugar yields have been reported in literature, few references exist on the comparison of the pretreatment costs. A quantitative economic analysis of some pretreatment methods was given by Eggeman and Elander (2005), in Table 6.3. More specific they focused on identifying the process economic impact of the different pretreatment approaches as related to capital cost investment. Their model assumes a 2,000 tn per day corn stover feed rate, which corresponds to nominally 50 Mmgal/yr, i.e. 190 million L/yr of ethanol production for the assumptions used in their models. Pretreatment direct fixed capital for hot water pretreatment was significantly lower than for the other cases. Lime was the alkali used. To generate the capital costs, the process model was used to establish the flows for each major piece of equipment, the equipment was then sized using standard engineering methods, and purchased costs were estimated using a combination of in-house methods and Questimate.

Table 6.3 Capital cost of different pretreatment processes, (raw material: corn stover, \$MM means million \$), [Eggeman and Elander, 2005]

Pretreatment method	Pretreatment direct fixed capital, \$MM
Hot water	4.5
Dilute acid	25.0
Alkali	22.3

It could be concluded that low-cost pretreatment reactors are often counterbalanced by higher cost pretreatment catalyst recovery or higher costs for the final product recovery (Alvira, et al., 2010). Furthermore, according to the 6.3 section, (Hsu et al., 1980; Chum et al., 1985; Choi, 1996; Sun and Cheng, 2002; Vessia, 2005; Mosier et al., 2005a; Balat et al., 2008; Kumar et al., 2009; Luterbacher et al., 2010; Raspolli-Galletti and Antonetti, 2011; Humbird et al., 2011), the examined alternatives for the first criterion take the following position: $\mathbf{A_1} \rightarrow \mathbf{A_4} \rightarrow \mathbf{A_3} \rightarrow \mathbf{A_2} \rightarrow \mathbf{A_5}$, (the arrow denotes ‘preferable to’ or ‘outranks’).

Conde-Mejía et al., 2012, analyzed the potential of several pretreatment methods for bioethanol production from lignocellulosic materials. Their simulations based on stoichiometric relations and yield data were conducted to evaluate the energy requirements of each pretreatment method. Lime was the alkali used. Energy was consumed for heating, cooling and power duties. Table 6.4 shows the Aspen Plus results expressed in energy consumption per tn of dry biomass. For the organosolvent pretreatment case, the energy required for the column was not included; however, it was evident that this method had the highest energy cost. In the steam explosion case saturated vapor was obtained from the heater, while for the dilute sulphuric acid hydrolysis case the output consisted of saturated liquid, at the corresponding temperature values. In this option, an additional feed stream with sulphuric acid was needed. Two flash units were used in order to simulate the alkali pretreatment. The first flash unit, operated at constant temperature (120^{o}C), simulated the mixing process of solids with lime solution, while the second unit was used to implement the temperature decrease and pressure drop after pretreatment. After this, filtering and washing steps were required. The experimental reports indicated that the solids were washed until the washing water was colourless; 1.5 tn of water per tn of dry biomass to the washer was added, which removed around 97% of lime from solids. For the organosolvent pretreatment a hydrous ethanol recovery system was included. A stoichiometric reactor was used to get the mass balance, followed by a flash unit to simulate the temperature decrease, keeping the vapor fraction equal to zero. A splitter was used to separate the dense phase from the black liquor mixture. The dense phase needed to be washed in order to maximize the ethanol recovery; the liquid phase from the washer was mixed with the black liquor. The stream from the mixer was sent to an ethanol recovery column; in the top of the column a mixture of ethanol–water was obtained, while the bottoms product consisted of a mixture of lignin and the main part of the hydrolysis liquid products. Finally, with the implementation of a flash unit followed by a filter, the xylose and lignin fractions were separated.

Table 6.4 Energy requirements for each pretreatment method without recycle usage, (MMBtu means million Btu's), [Conde-Mejía et al., 2012]

Pretreatment method	Heating (MMBtu/ dry biomass tn)	Cooling water (MMBtu/ dry biomass tn)	Total (MMBtu/dry biomass tn)
Steam explosion	2.66	0.79	3.45
Dilute sulphuric acid hydrolysis	6.14		6.14
Alkali	3.95	3.76	7.71
Organosolve	7.78	3.14	10.92

Moreover, as regards the second criterion *f*$_2$: operating cost (mainly energy, raw material price) according to the section 6.3, (Chum et al., 1985; Choi, 1996; Avellar and Glasser, 1998; Jeffries and Jin, 2000; Hamelinck et al., 2005; Carvalheiro et al., 2008; Humbird et al., 2011; Sidiras et al., 2011a), the examined alternatives for the second criterion take the following position: $\mathbf{A_2 \rightarrow A_1 = A_3 \rightarrow A_4 \rightarrow A_5}$.

In Table 6.5 capital and operating cost of three different pretreatment processes of lignocellulosic materials, for the same capacity in order to produce bio-ethanol, are presented.

Table 6.5 Capital and operating cost of different pretreatment processes of lignocellulosic materials, (€MM means million €)

Pretreatment method	Capital cost, €MM	Operating cost, €MM
Hot water	27.01	43.02
Dilute acid	50.22	34.91
Organosolve	29.67	54.65

As regards the third criterion *f*$_3$: health occupational (including safety), according to the section 6.3, (Avellar and Glasser, 1998; Hamelinck et al., 2005; Mosier et al., 2005a; Galbe and Zacchi, 2007; Carvalheiro et al., 2008; Balat et al., 2008; Kumar et al., 2009; She et al., 2009; Romaní et al., 2010; Sidiras et al., 2011a; Raspolli-Galletti and Antonetti, 2011; Menon and Rao, 2012), the examined alternatives for the third criterion take the following position: $\mathbf{A_1 \rightarrow A_3 \rightarrow A_5 \rightarrow A_4 \rightarrow A_2}$.

As regards the fourth criterion *f*$_4$: reliability, according to the section 6.3, (Chum et al., 1985; Holtzapple et al., 1989; Choi and Cloud, 1992; McMillan, 1994; Botello et al., 1999; Mosier et al., 2005a; Taherzadeh and Karimi, 2007; Nabarlatz et al., 2007; Jorgensen et al., 2007; Lee et al., 2009; Raspolli-Galletti and Antonetti, 2011; Al-Majed et al., 2012; Li and Wei, 2012a; Li and Wei, 2012b), the examined alternatives for the fourth criterion take the following position: $\mathbf{A_5 \rightarrow A_2 \rightarrow A_1 \rightarrow A_3 = A_4}$.

As regards the fifth criterion *f*$_5$: environmental friendliness (through Life Cycle Assessment), according to the section 6.3, (Hsu, 1996; Choi, 1996; Avellar and Glasser, 1998; Galbe and Zacchi, 2007; Balat et al., 2008; Carvalheiro et al., 2008; She et al., 2009; Lee et al., 2009; Kumar et al., 2009; Romaní et al., 2010; Raspolli-Galletti and Antonetti, 2011; Kumar and Murthy, 2012), the examined alternatives for the fifth criterion take the following position: $\mathbf{A_1 \rightarrow A_2 \rightarrow A_3 = A_4 \rightarrow A_5}$.

As regards the sixth criterion f_6: adsorption efficiency, according to the section 6.3, (measurements in this study; Ibrahim et al., 2009; 2010), the examined alternatives for the sixth criterion take the following position: $\mathbf{A_5 \rightarrow A_1 \rightarrow A_2 \rightarrow A_3 \rightarrow A_4}$.

As regards the seventh criterion f_7: widely spread (available) know-how, (maturity of technology), according to the section 6.3, (Root et al., 1959; Chum et al., 1985; Fox et al., 1989; Holtzapple et al., 1989; Elshafei et al., 1991; Choi and Cloud, 1992; Soto et al., 1994; McMillan, 1994; Botello et al., 1999; Taherzadeh and Karimi, 2007; Jorgensen et al., 2007; Al-Majed et al., 2012), the examined alternatives for the seventh criterion take the following position: $\mathbf{A_5 \rightarrow A_1 \rightarrow A_2 = A_3 \rightarrow A_4}$.

Hamelinck et al., 2005, used in their research as base feedstock hybrid poplar, a representative hard wood. They compared various pre-treatment (lignin removal and hemicellulose hydrolysis) options to produce ethanol (Table 6.6). Commercially availability indicates the maturity of each pretreatment technology.

Table 6.6 Comparison of various pre-treatment, (lignin removal and hemicellulose hydrolysis), options [Hamelinck et al., 2005]

Pre-treatment method	Chemicals	Temperature °C	Reaction time (min)	Xylose yield (%)	Costs	Commercially available
Steam explosion	–	160–260	2	45–65	Nil	In 2–5 years
Liquid hot water	None	190–230	45s–4 min	88–98%	Nil	In 5–10 years
Dilute acid hydrolysis	Acid	> 160	2–10	75–90	+	Now
Alkaline hydrolysis	Base	–	–	60–75	++	Now

+ Indicates that the effect is advantageous (less expensive).

As regards the eighth criterion f_8: contribution to sustainability at local level (including the Industrial Ecology aspect), according to the section 6.3, (Fan et al., 1987; Choi and Cloud, 1992; Bjerre et al., 1996; Avellar and Glasser, 1998; Teas et al., 2001; Sun et al., 2002; Deschamps et al., 2003; Adebajo et al., 2003; Mosier et al., 2005b; Jorgensen et al., 2007; Ruiz et al., 2008; Viola et al., 2008; Carvalheiro et al., 2008; Zhao et al., 2009; Kumar et al., 2009; Romaní et al., 2010; Sills and Gossett, 2011; Sidiras et al., 2011a; Raspolli-Galletti and Antonetti, 2011), the examined alternatives for the eighth criterion take the following position: $\mathbf{A_1 \rightarrow A_2 \rightarrow A_3 = A_4 \rightarrow A_5}$.

Finally, as regards the ninth criterion *f*$_9$: marketability within a wider network (depended mainly on ageing), according to the section 6.3, the examined alternatives for the ninth criterion take the following position: $\mathbf{A_5 \rightarrow A_1 = A_2 = A_3 = A_4}$.

The choice of the optimum pretreatment process depends on the feedstocks and its economic assessment and environmental impact. Menon and Raio, 2012, discussed and compared pretreatment strategies with the advantages, drawbacks and techno-economics data. Table 6.7 illustrates some of the most promising pretreatment categories that can be commercialized for the biofuel industry. However, none of those can be declared outstanding as each pretreatment has its intrinsic advantages and disadvantages.

Table 6.7 Most promising pretreatment technologies, (H: High and L: Low), [Menon and Rao, 2012]

Method of pre-treatment	Sugar yield	Inhibitor formation	Byproduct generation	Reuse of chemicals	Applicability to different feedstock's	Equipment cost	Success at pilot scale	Advantages	Limitations & disadvantages
Liquid hot water	H	H	L	---	---	---	Yes	Removal of hemicellulose making enzymes accessible to cellulose	Long residence time, less lignin removal
Mineral acids	H	H	H	Yes	Yes	H	Yes	Hydrolysis of cellulose and hemicellulose; alters lignin structure	Hazardous, toxic and corrosive
Alkali	H	L	H	Yes	Yes	---	Yes	Removal of lignin and hemicellulose; increases accessible surface area	Long residence time; irrecoverable salts formed
Organosolv	H	H	H	Yes	Yes	H	Yes	Hydrolyze lignin and hemicellulose	Solvents needs to drained, evaporated, condensed and reused

Data from Tables 6.3, 6.4, 6.5, 6.6 and 6.7 were used for the above mentioned comparison of the alternatives.

6.5 Implementation - interpretation of results

6.5.1 Implementation

The methodology described above is implemented in the case of multi criteria ranking of oil adsorbents obtained from modified lignocellulosic or commercial adsorbents. The choice of this category of adsorbent materials was based on the high applicability, low cost, environmental friendliness etc.

The alternatives examined were: autohydrolyzed wheat straw, A_1; sulfuric acid-hydrolyzed wheat straw, A_2; sodium hydroxide treated wheat straw, A_3; organosolv treated wheat straw, A_4; polypropylene oil adsorbent pads, A_5. The criteria used were: capital cost, f_1; operating cost, f_2; health occupational, f_3; reliability, f_4; environmental friendliness, f_5; adsorption efficiency, f_6; maturity of technology, f_7; contribution to sustainability at local level, f_8; marketability within a wider network, f_9.

Alternative A_1, based on autohydrolysis of wheat straw, was ranked in the first place since exhibited low capital and operating cost, (f_1) and (f_2), respectively. Furthermore A_1 showed high health occupational (f_3) and environmental friendliness (f_5). Finally, A_1 alternative contributed better than the other alternatives to sustainability at local level (f_8). On the other hand, alternatives A_5 and A_4, polypropylene oil adsorbent pads and organosolv pretreatment of wheat straw, respectively, were ranked in the pre-last and last places, since they lacked: A_5 in capital and operating cost, (f_1) and (f_2), respectively, in environmental friendliness (f_5) and in sustainability at local level (f_8); and A_4 in health occupational (f_3), in reliability (f_4), in adsorption efficiency (f_6:), in maturity of technology (f_7) and in marketability within a wider network ($f_{9.}$)

Alternatives A_2 and A_3, based on sulfuric acid-hydrolysis of wheat straw and on sodium hydroxide pretreatment, respectively, were ranked in the second and third places, as A_2 showed low operating cost (f_2), high reliability (f_4), environmental friendliness (f_5) and sustainability at local level (f_8), while A_3 exhibited relatively low capital and operating cost, (f_1) and (f_2), respectively, and high health occupational (f_3).

In implementing the study purpose, the scores of the alternatives evaluation were filled-in by the author. Scoring range was the interval from 0 to 5. The alternatives' scores as well as the weights of the assessment criteria entered into the MCA table.

6.5.2 Interpretation of results

The MCA resulted in ranking the alternatives by classifying them according to author's scores. The 'rule of thumb' to rank the alternatives was 'the higher the total scores the better the alternative'. The preference matrix, in which the pair wise comparisons between all the alternatives are referred to as outranking measures, is shown in Table 6.8.

Table 6.8 Preference Matrix of the alternatives

	wi	A_1	A_2	A_3	A_4	A_5	A_1	A_2	A_3	A_4	A_5
f_1	18%	5	3.2	3.3	4.6	1.1	0.900	0.567	0.594	0.835	0.200
f_2	13%	4.2	5	4.2	3.5	1.1	0.544	0.650	0.546	0.456	0.141
f_3	9%	5	1	4	2	3	0.450	0.090	0.360	0.180	0.270
f_4	11%	3	4	2	2	5	0.330	0.440	0.220	0.220	0.550
f_5	10%	5	4	3	3	2	0.500	0.400	0.300	0.300	0.200
f_6	13%	4	3	2	1	5	0.520	0.390	0.260	0.130	0.650
f_7	8%	4	3	3	2	5	0.320	0.240	0.240	0.160	0.400
f_8	7%	5	4	3	3	2	0.350	0.280	0.210	0.210	0.140
f_9	11%	2	2	2	2	3	0.220	0.220	0.220	0.220	0.330
	100%			**Total**			**4.134**	**3.277**	**2.950**	**2.711**	**2.881**

f_1, capital cost
f_2, operating cost
f_3, health occupational
f_4, reliability
f_5, environmental friendliness
f_6, adsorption efficiency
f_7, maturity of technology
f_8, contribution to sustainability at local level
f_9, marketability within a wider network

The above numbers represent the pair wise comparison scores among the alternatives produced by the MCA. To arrive at aggregate preference scores the pair wise comparison' scores are summarized for each row. The greatest aggregate score indicates the most preferable alternative; the second greatest score the secondly preferable and so on. In this study the final ranking of the alternatives in order of preference is the following: $\mathbf{A_1} \rightarrow \mathbf{A_2} \rightarrow \mathbf{A_3} \rightarrow \mathbf{A_5} \rightarrow \mathbf{A_4}$, the arrow denotes 'preferable to' or 'outranks'. This means that alternative A_1 (autohydrolyzed wheat straw) is the most preferred of all the alternatives for the selection of oil adsorbents obtained from modified lignocellulosic or commercial adsorbents. Therefore, alternative A_2 (sulfuric acid-hydrolyzed wheat straw) comes second in preference, followed by A_3 (sodium hydroxide treated wheat straw), A_5 (polypropylene oil adsorbent pads) and A_4 (organosolv treated wheat straw) last of all.

6.6 Discussion

The MCA technique employed was based on the outranking relations techniques. In this study, dealing with selecting of oil adsorbents obtained from modified lignocellulosic or commercial adsorbents, the MCA results suggest as first-best alternative the $A_{1,}$ second-best A_2, third A_3 then A_5 and finallyA_4. In other words, MCA indicates the order of the alternatives in terms of preference; i.e. it only indicates the most preferable ‘solution’ under given circumstances. It cannot decide on behalf of the decision-maker; nor can any other decision aiding technique or method. It is the decision-maker who’s responsible to select the best solution(s) for the problem at hand. Taking into account that any solution should be economically, environmentally, socially and technically feasible, namely both efficient and effective, the decision-maker has to use a managerial procedure in order to arrive at a more holistic decision.

Nevertheless, whatever the designation of the oil adsorbent selection might be, the application of MCA in order to amplify the decision-making procedure should be thought as of crucial importance. MCA contributes to the decision-maker in that it expands the decisional space to include both quantitative and qualitative information leading to a more ‘holistic’ consideration of the problem at hand. MCA primarily results to a preference ranking of the alternatives and secondarily contributes to valuable insights by the decision-maker. In the present study, MCA to the selection of oil adsorbent obtained from modified lignocellulosic or commercial adsorbents showed that this recipe could provide reasonable results for decision-makers, even at the theoretical level. In conclusion, the optimum conditions of pre-treatment strictly depend on the characteristics of each raw material (composition, harvesting time, water content, etc.) as well as on the final purpose of the process itself (bio-fuels, chemicals production, etc.). Technoeconomic studies which compare the different technologies have been reported only for bio-ethanol production from different lignocellulosic materials (Raspolli-Galletti and Antonetti, 2011).

CHAPTER 7
MATERIALS AND METHODS

7.1 Materials

Modification experiments were performed using wheat and barley straw. The wheat straw obtained from Thessaly in Central Greece had a moisture content of 8.75% w/w. It was chopped with hedge shears in small pieces and the fraction with sizes 1-2 cm (representing more than 95% of the raw total wheat straw) was collected by sieving. This fraction was chosen because it is more suitable for scale up of the process. The composition of wheat straw was given in Table 7.1 (Sidiras et. al., 2014).

The barley straw used was also obtained from Thessaly area, as a suitable source for full-scale industrial applications. The moisture content of the material when received was 8.5% w/w; after screening, the fraction with particle sizes between 10 and 20 mm was isolated. The composition of the raw material was as follows (expressed in % w/w on a dry weight basis): 31.7% cellulose, 21.1% hemicelluloses (polysaccharides 52.8% w/w), 8.2% acid-insoluble lignin, 11.4% ash and 27.7% extractives and other components. Cellulose crystallinity was 73.3%, and the fraction of non-easily hydrolysable hemicelluloses was 0.405 (Sidiras et. al., 2011c).

Table 7.1 Composition of untreated and autohydrolyzed (200°C, 10 min) wheat straw

Component	% w/w on dry wheat straw weight basis	
	Untreated	Autohydrolyzed (200°C, 10 min)
Cellulose	32.7	55.3
Hemicelluloses	24.5	1.3
Xylose	19.3	1.1
Arabinose	2.7	0.1
Acetyl groups	2.5	0.1
Klason acid-insoluble lignin	16.8	30.5
Ash	4.7	1.6
Extractives	6.2	2.1
Others	15.1	9.1
XRD degree of crystallinity of cellulose	79.5	82.1

The adsorbency tests, (pure liquids and oil spills), were performed using, untreated/ pretreated wheat straw, (barley straw was used only in pure liquids tests), commercial polypropylene oil adsorbent pad “Scorpion P-200” and pom-poms oil trap (both manufactured by New Naval Ltd located in Piraeus, Greece), as sorbents. In pure water adsorbency tests freshwater (stream water or lake water) was used. In oil adsorbency tests (pure oils and oil spills) diesel 10 PPM and crude oil provided by Hellenic Petroleum S.A. of predetermined quality specifications (Table 7.2) were used as oily media. The various adsorption tests were conducted at pH 7.7 ± 0.1 as regards freshwater and 7.9 ± 0.1 as regards seawater. These pH values are comparable with the literature values which are in most cases 6-8 (Srinivasan and Viraraghavan, 2008; Ibrahim et al., 2009; Ibrahim et al., 2010; Angelova et al, 2011).

Table 7.2 Quality specifications of diesel 10 PPM and crude oil

Properties	Units	Results	Methods
Diesel oil quality specifications			
Density at 15°C	kg/m^3	823.0	EN ISO 12185
Color		L0.5	ASTM D 1500
% (v/v) Recovered at 250°C	%v/v	35.3	EN ISO 3405
% (v/v) Recovered at 350°C	%v/v	94.6	EN ISO 3405
95% (v/v) Recovered	°C	359.0	EN ISO 3405
Flash point	°C	61.5	EN ISO 2719
Sulfur content	mg/kg	2.2	EN ISO 20846
Copper strip corrosion (3 hr at 50°C)	Class	1a	EN ISO 2160
CFPP	°C	-17	EN 116
Viscosity at 40°C	cST	2,772	EN ISO 3104
Water content	mg/kg	45	EN ISO 12937
Cetane number		54.0	EN ISO 5165
Cetane index		57.9	EN ISO 4264
Ash content	% m/m	0.003	EN ISO 6245
Carbon residue (on 10% distillation residue)	%m/m	0.01	EN ISO 10370
Total contamination	mg/kg	5.0	EN 12662
Oxidation stability	g/m^3	3.4	EN ISO 12205
Polycyclic aromatic hydrocarbons	%m/m	0.6	EN 12916
Lubricity, corrected (wsd 1.4) at 60°C	Mm	435	EN ISO 12156-1
Crude oil quality specifications			
Density at 15°C	kg/m^3	860.0	EN ISO 12185
Water content	mg/kg	250	EN ISO 12937

In oil spills tests with the presence of substitute seawater; water was prepared according to the ASTM D1141-98 (1998) method, while in these with the presence of seawater; water was derived from Saronicos Golf (close to Piraeus Port). In oil spills (diesel oil/ crude oil) tests that were performed with the presence of chemical dispersant, Marichem oil spill dispersant (Marichem Marigases Hellas S.A.) was used. It is a 3rd generation non toxic liquid dispersant, applicable to mineral, crude, fuel and lubricant oils, kerosene and white spirits. It is a low viscosity product containing surface-active wetting agents combined with a biodegradable oil-soluble, non-ionic emulsifying agent. Its density (g/mL) was 1.00-1.05 g/cm^3 at 20°C, flash point at 90°C and its pH was 7.

7.2 Modification Processes

A 3.75-L batch reactor PARR 4843 was used in order to modify the materials described in sub-chapter 7.1 (Fig. 7.1).

Fig. 7.1 The 3.75-L batch reactor PARR 4843

Auto-hydrolysis Process

The materials, mentioned in sub-chapter 7.1, were auto-hydrolyzed. The isothermal hydrolysis time was t = 0, 10, 20, 30, 40, and 50 min (not including the non-isothermal preheating and cooling periods). The reaction was catalyzed by the organic acids that were produced by the materials itself during auto-hydrolysis at a liquid-to-solid ratio of 20:1. The volume of the liquid phase (water) was 2000 mL and the solid material dose of wheat and barley straw was 100 g (i.e. 91.25 g on dry basis). The stirring speed for straw pretreatment was 50 rpm. The reaction ending temperatures of T=160, 180, 200 and 240°C were reached: for wheat straw after 43, 50, 62 and 82 min and for barley straw after 44, 47, 66 and 80 min of preheating time values, respectively.

The auto-hydrolysis products were filtered using a Buchner filter with Munktell paper sheet (grade 34/N) to separate the liquid phase from the solid phase (Fig. 7.2). The solid residues were washed with water until neutral pH. The initial filtrate pH was 3.82-5.87 for wheat straw and 3.98-5.35 for barley straw depending on the auto-hydrolysis severity. The solid residues were dried at 110°C for 24 hr.

Fig. 7.2 Autohydrolysis products filtration using a Buchner filter

Acid hydrolysis Process

The materials, mentioned in sub-chapter 7.1, were acid hydrolyzed. The acid hydrolysis time was t = 0, 10, 20, 30, 40, and 50 min (not including the preheating time; preheating time must be added to these isothermal reaction time-periods to give the ‘Acid hydrolysis Time’, t). The reaction was catalyzed by sulfuric acid 0.045 N during acid hydrolysis at a liquid-to-solid ratio of 20:1. The volume of the liquid phase (water) was 2000 mL and the solid material dose of wheat and barley straw was 100 g (i.e. 91.25 g on dry basis). The stirring speed for the straw was 50 rpm. The reaction ending temperatures of T= 160°C, 180°C, 200°C, and 220°C were reached: for wheat straw after 45, 53, 62 and 70 min and for barley straw after 45, 53, 62 and 70 min of preheating time values, respectively.

The acid hydrolysis products were filtered using a Buchner filter with Munktell paper sheet (grade 34/N) to separate the liquid phase from the solid phase (Fig. 7.2). The solid residues were washed with water until neutral pH. The initial filtrate pH was 2.33-2.47 for wheat straw and 2.11-2.95 for barley straw depending on the acid hydrolysis severity. The solid residues were dried at 110°C for 24 hr.

7.3 Batch adsorption experiments procedure

Adsorption rate batch experiments were conducted in a 2 L that is filled with 300 ml of oil (diesel oil/ crude oil). The sorbent weight was 4 g of wheat straw: untreated wheat straw (UWS) and autohydrolyzed wheat straw at 180^{o}C for 50 min (AWS). The container was then placed on a shaker table, at a frequency of 150 rpm for 2, 5, 15, 30, 60, 120, 240 and 1440 min and allowed to settle for a period of 2 min for keeping the lignocellulosic material in suspension. The reactor, containing 300 ml diesel/ crude oil solution, was placed into a water bath to keep temperature constant at the desired level (23^{o}C). For the measurement of the oil adsorbency the procedure described in the next sub-chapter, was followed. The effect of contact time (t in min) on the uptake of oil was studied in triplicate batch experiments with the mean of the three runs being used for calculations.

7.4 Analytical Techniques

Following the technique proposed by Saeman et al. (1945), the lignocellulosic materials were hydrolyzed to glucose and reducing sugars in nearly quantitative yields; the filtrates were analyzed for glucose using an enzymatic test and for reducing sugars using the Somogyi technique (1952). Based on these results the cellulose and hemicelluloses content of the adsorbents were estimated. The quantitative saccharification filtrates were analyzed for glucose, xylose, and arabinose using high-performance liquid chromatography (HPLC, Agilent 1200) with an Aminex HPX-87H Column, a refractive index detector, and 5 mM H_2SO_4 in water as the mobile phase. Cellulose was measured as glucan, and hemicelluloses were measured as xylan and arabinan. Finally, the acid-insoluble lignin (Klason lignin) was determined according to the Tappi T222 om-88 method (1997).

The degree of crystallinity of wheat straw cellulose was measured by means of X-ray diffraction (Segal et al., 1959). The XRD pattern was measured on by a

SIEMENS D5005 X-Ray Diffractometer using Ni-filtered CuKa (0.154 nm) radiation at 45 kV and 40 mA and continuous scan mode. The XRD pattern was recorded in the scan range 2θ=5-70, at scan rate step=0.04^{o}, dwell time=3 sec, i.e. total scan time approximately 1 hr and 30 min.

The scanning electron microscope (SEM) used for the study of the untreated/ pretreated by auto-hydrolysis wheat straw was a JEOL JSM-6700F Field Emission Scanning Electron Microscopy. The SEM tests were carried out on samples which were Pt coated (5 nm). The magnifications were 750, 7,500 and 50,000, respectively.

Fourier transform infrared (FTIR) spectra were obtained using a spectroscope (MAGNA-IR 750 Spectrometer, Serrie II, Nicolet). The sampling technique used herein was diffuse reflectance. The samples were scanned for wave-number 650-4,000 cm^{-1}.

In the case of pure: water and diesel oil/crude oil, the calculation of the adsorptive capacity was achieved by measuring:

water adsorbency (ability of a material to absorb water) as a ratio of water adsorbed to dry adsorbent weight as follows: *Water Adsorbency* = S_W/S_O

where: S_O = initial dry adsorbent weight, S_{WT} = weight of adsorbent samples at end of water test, $S_W = (S_{WT} – S_O)$ net water adsorbed, and

oil adsorbency (ability to absorb an oily medium) as the ratio of oil adsorbed to dry adsorbent weight: *Oil Adsorbency* = S_S/S_O

where: S_O = initial dry adsorbent weight, S_{ST} = weight of adsorbent samples at end of oil test, $S_S = (S_{ST} – S_O)$ net oil adsorbed.

Therefore water and oil adsorbencies were countered as g/g. The procedure for determining the water and the oil adsorbencies was done according to the F726-12 (2012) ASTM method.

In the case of oil (diesel oil/ crude oil) spills tests, the water in adsorbed oil/water mixture was determined by distillation according to the ASTM D95-05 (2005) method. The water and oil adsorbency was the amount of oil and water adsorbed per gram of adsorbent, respectively. The total adsorbency was the sum of oil and water adsorbency. The relative adsorbency was the fraction of oil compared to the oil/water mixture adsorbed by the sorbent. In diesel oil spills (DOS) the relative diesel oil adsorbency (RDA) while in crude oil spills (COS) the relative crude oil adsorbency (RCA) were determined, respectively.

Procedure and laboratory equipments of the adsorption experiments

Pure liquids experiments

The following materials and laboratory equipments were used in these experiments: 4 g of adsorbent (wheat/barley straw untreated/pretreated, adsorbent pad and pom-poms oil trap), 1 L of freshwater, 300 ml of oil (diesel oil/crude oil), 2 L jar, a metal sieve, a plastic bucket, a precision scale, a shaker table and 1 L glass cylinder. For the measurement of the water and oil (diesel oil/ crude oil) adsorbencies the following procedure was followed: an adsorbent sample of 4 g was first weighed then placed in a 2 L jar that is filled with 1 L or 300 ml of freshwater or oil (diesel oil/crude oil), respectively, measured in a 1 L glass cylinder and sealed (Fig. 7.3).

Fig. 7.3 Water (left), Diesel oil (middle) and Crude oil (right) adsorbency testing experiments according to ASTM F 726-2012 method

The container was then placed on a shaker table, at a frequency of 150 rpm for 15min and allowed to settle for a period of 2 min. The contents of the jar were strained through a metal sieve, (that was first weighed), appropriate fitted in a bucket so the liquids poured inside it, drained for a 30 s period, and then weighed, (metal sieve and its contained adsorbent samples). Finally, the initial weight of the sieve was subtracted and the weight of adsorbent samples at end of water/ oil tests was resulted. The water and oil (diesel oil/crude oil) pick-up ratios were calculated from the weight measurements described in this sub-chapter. All tests were triplicate with the mean of the three runs being used for calculations.

Oil spills experiments

The following materials and laboratory equipments were used in these experiments: 4 g of adsorbent (wheat straw untreated/pretreated, adsorbent pad and pom-poms oil trap), 1 L of freshwater/seawater/substitute seawater, 50 ml of oil spill (diesel oil/crude oil), 100 ml of diesel oil as solvent-carrier liquid, 2 L jar, a metal sieve, a plastic bucket, precision scale, a shaker table, 1 L glass cylinder, a porcelain plate a small porcelain boiling nuclei, a typical assembly with glass still (Fig. 7.4) and a silicone oil bath with thermostat.

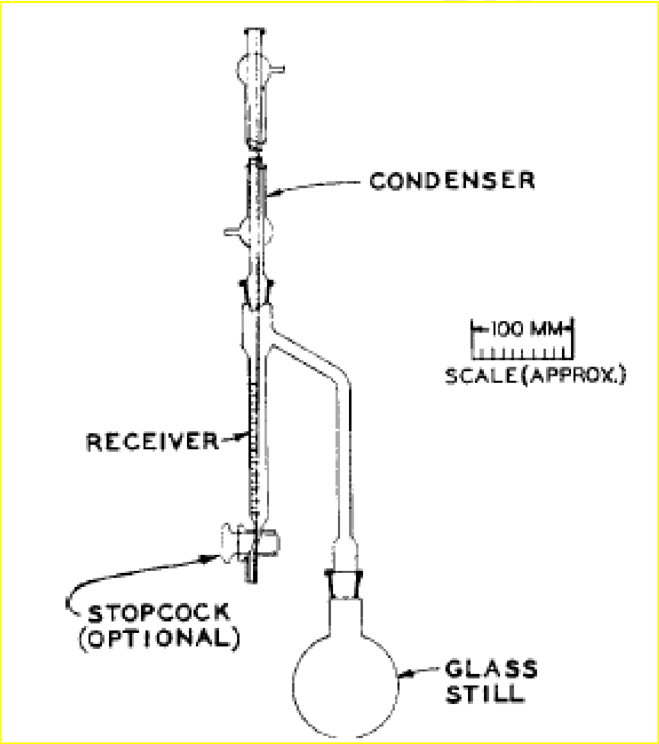


Fig. 7.4 A typical assembly with glass still

For the measurement of the water in adsorbed oil/water mixture the following procedure was followed: an adsorbent sample of 4 g was first weighed then placed in a 2 L jar that is filled with 1 L of freshwater/seawater/substitute seawater and 50 ml of oil spill (diesel oil/crude oil), respectively, measured in a 1 L glass cylinder and sealed. The container was then placed on a shaker table, at a frequency of 150 rpm for 15 min and allowed to settle for a period of 2 min. The contents of the jar were strained through a metal sieve, (that was first weighed), appropriate fitted in a bucket so the liquids poured inside it, drained for a 30 s period, put in a porcelain plate, (that was first weighed), and then weighed (porcelain plate and its contained adsorbent samples). Finally, the initial weights of the sieve and the plate were subtracted and the weight of adsorbent samples at end of oil (diesel oil/ crude oil) spills tests was resulted.

These adsorbents samples were put and heated, (in a silicone oil bath at 130°C for four hours), under reflux in a glass still which contained small porcelain boiling nuclei, (to avoid potential explosions), and 100 ml of diesel oil as solvent-carrier liquid that was co-distilled with the water in the sample. Condensed solvent and water were continuously separated in a trap, the water was settling in the graduated section of the trap and the solvent was returning to the still. The adsorbency and the relative adsorbencies (RDA and RCA) were calculated as described in this sub-chapter.

CHAPTER 8
MODIFICATION RESULTS AND DISCUSSION

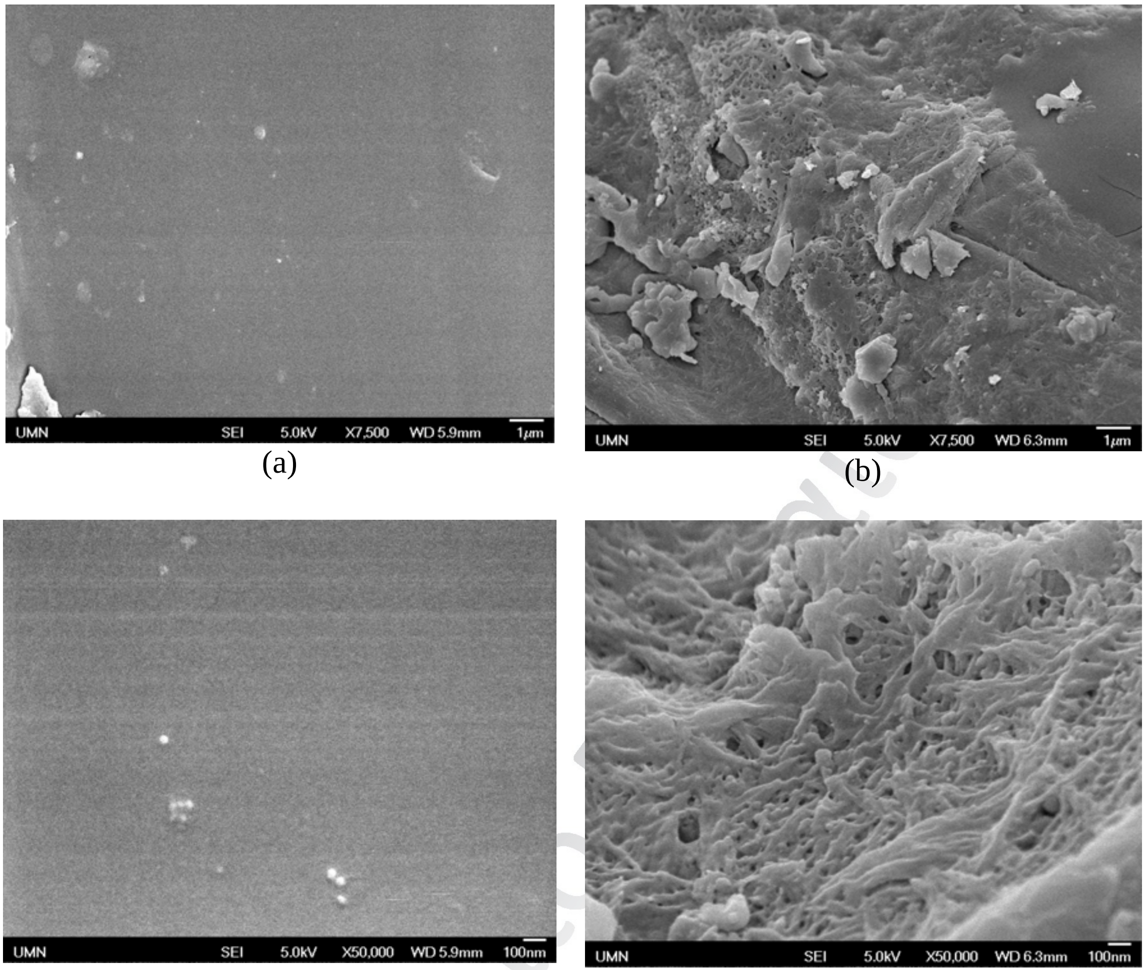
8.1 Introduction

Agricultural residues are not used in food industry and so far have not developed many alternative uses. Moreover, the problem of disposal of agricultural residues makes research into new uses for them even more attractive. Literature survey, reported in the fifth chapter of the thesis, shows that many researchers used untreated/ pretreated straw (barley, wheat, rice) as adsorbents for diminishing an oil-products spill in seawater.

In this study, the modification of materials such as wheat straw and barley straw was examined in order to detect if the pretreatment improves the initial adsorption capacities of these materials. Auto-hydrolysis and acid hydrolysis (sub-categories of hydrothermal treatment) were selected as modification processes to cover a gap in the literature as they have so far never used again to obtain adsorbents with relatively high sorption capacity, biodegradability and cost-effectiveness for cleaning an oil spill in seawater. The experimental procedure took place in the Laboratory of Simulation of Industrial Processes of the University of Piraeus, except SEM and FTIR.

8.2 SEM and FTIR measurements of untreated and pretreated materials

The SEM micrographs for untreated and auto-hydrolyzed wheat straw are shown in Fig. 8.1. The change of the adsorbent surface texture due to auto-hydrolysis is more than obvious. The texture of the auto-hydrolyzed wheat straw is very rough while the texture of the untreated material is very smooth. The rough texture results to the improved adsorptivity of the material. The FTIR spectra of the untreated wheat straw and of the auto-hydrolyzed one are given in Fig. 8.2. The comparison of the FTIR spectrums shows that some peaks were shifted due to auto-hydrolysis as is shown in Table 8.1. The wave-number values for untreated wheat straw were very close to those reported by Han et al., (2010) and Jiang et al., (2009). SEM and FTIR were conducted at the Laboratory of 'Tsapatsis Research Group', Department of Chemical Engineering and Materials Science, University of Minnesota.



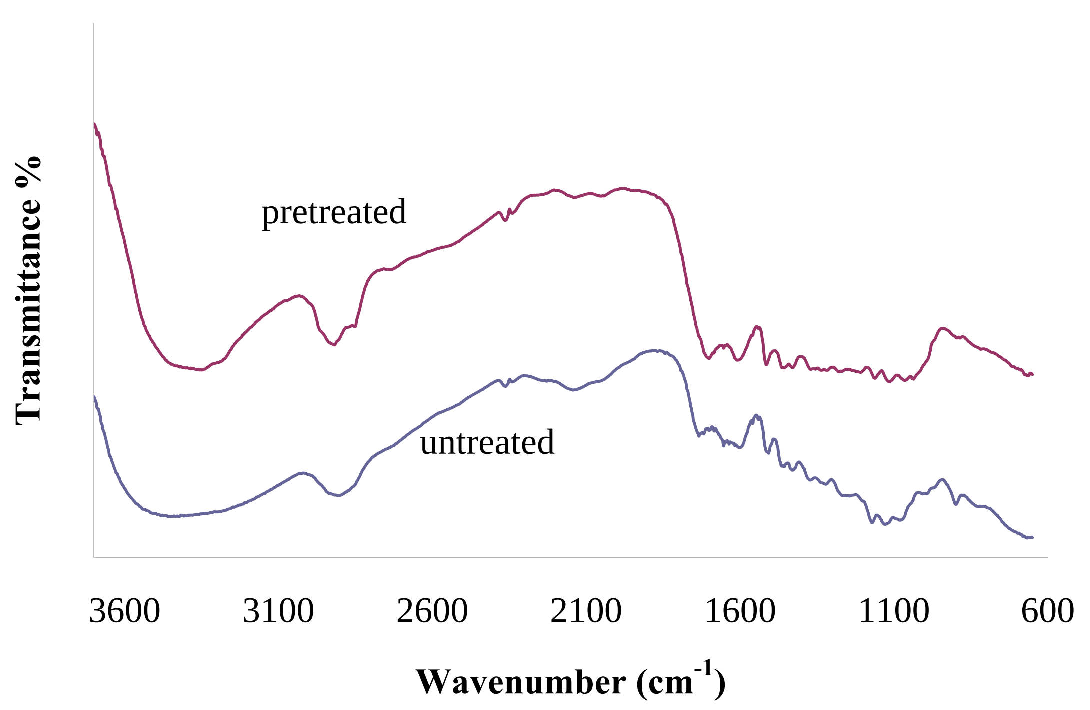
(a) (b)

(c) (d)

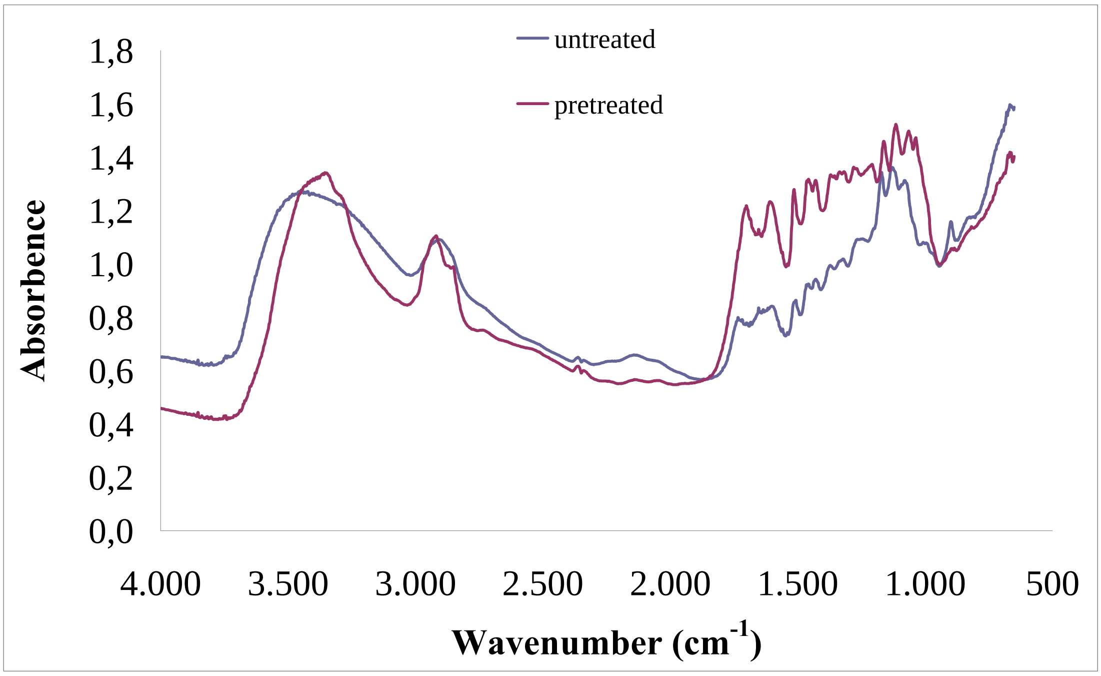
Fig. 8.1 SEM micrographs for untreated (a, c) and autohydrolyzed (240^{o}C, 50 min + 80 min preheating period) wheat straw (b, d)

Table 8.1 FTIR of untreated and autohydrolyzed (240^{o}C, 50 min) wheat straw

Frequency (cm^{-1})		Differences (cm^{1})	Assignment
Untreated	Pretreated (autohydrolysis 240^{o}C, 50 min)		
3,464	3,369	95	-OH stretching of phenol group
2,914	2,935	-21	C-H asymmetric stretching of methyl group
-	2,862	-	C-H symmetric stretching of methyl group
1,736	1,709	27	C= O stretching of aldehyde group
1,610	1,616	-6	C= O stretching of ketones
1,520	1,518	2	C =C stretching of aromatic rings
1,433	1,446	-13	-CO-OH stretching of carboxyl group in lignin
1,377	1,375	2	C-H bending of methyl group
1,255	1,225	30	C-O stretching of phenolic group
1,136	1,122	14	C-O-C antisymmetric bridge in hemicelluloses and cellulose
1,086	1,047	39	C-O band of lignin
906	-	-	C-H deformation



(a)

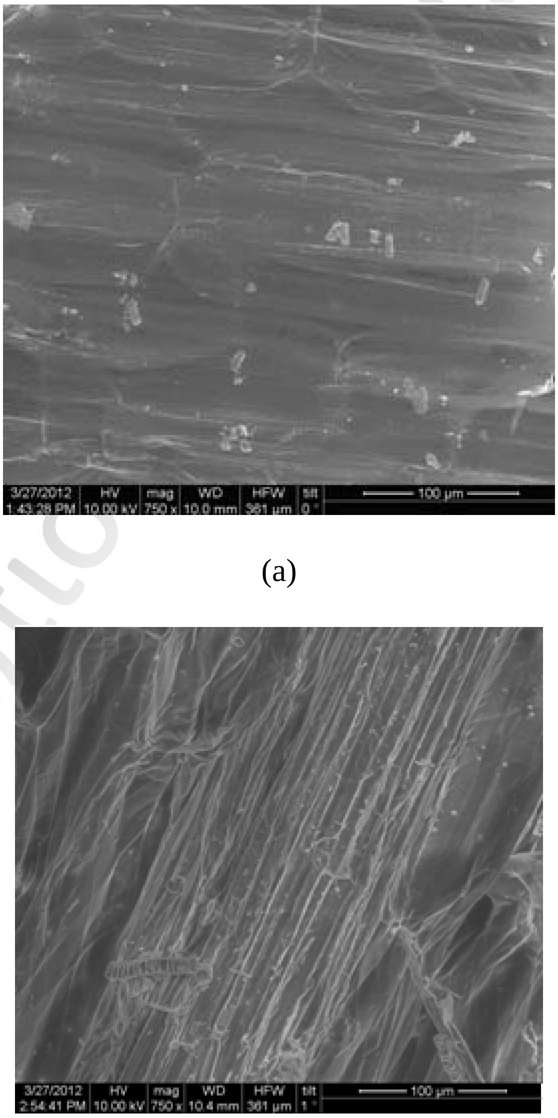


(b)

Fig. 8.2 FTIR spectra of untreated and auto-hydrolyzed (240°C, 50 min + 80 min preheating period) wheat straw; (a) transmittance and (b) absorbence = -ln of transmittance

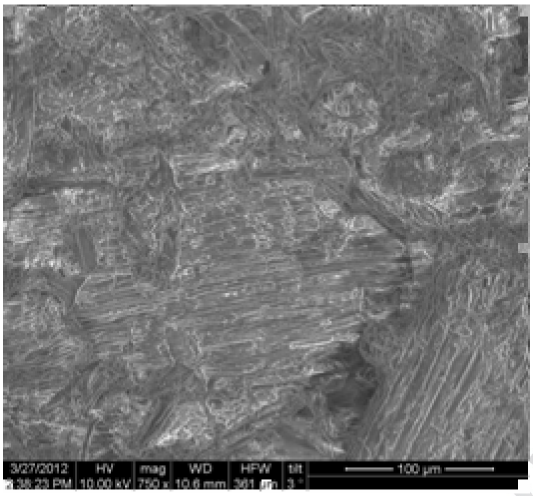
The untreated/ pretreated by auto-hydrolysis barley straw is shown in Fig. 8.3.

Fig. 8.3 Untreated (left) and pretreated by auto-hydrolysis (right) barley straw



(a)

(b)



(c)

Fig. 8.4 SEM micro-graphs of barley straw (a) untreated (b) treated with 0.045 N H_2SO_4 at 160°C for 30 min and (c) treated with 0.045 N H_2SO_4 at 220°C for 30 min. Magnification 750 X

Fig. 8.5 Untreated (up left) and pretreated by acid hydrolysis (down right) barley straw

The study of untreated/ pretreated by acid hydrolysis barley straw samples by scanning electron microscopy, SEM, (Fig. 8.4) was conducted at the Division of Materials Science of the National Center for Scientific Research ‘Demokritos’ using an FEI INSPECT SEM equipped with an EDAX super ultra thin window analyzer for energy dispersive X-ray spectroscopy (EDS).

The magnification was 750. The untreated and pretreated by acid hydrolysis barley straw is shown in Figure 8.5.

8.3 Auto-hydrolysis of wheat straw

The detailed simulation of the straw (wheat and barley) modification process (auto-hydrolysis and acid-hydrolysis) can be performed using a modified complicated simulation model for dilute acid hydrolysis of lignocellulosic materials described in earlier work (Sidiras and Koukios, 1989; Sidiras, 1998; Sidiras et al., 2011b).

The hydrolysis process solid residue yield (SRY) of the wheat straw (dry weight of product % w/w of the original dry material) was estimated. A new Severity Factor log R_o was introduced herein taking into account the relevant literature (Abatzoglou et al., 1992; Sidiras, 1998).

The adsorbency-values were simulated by the proposed novel model incorporating the auto-hydrolysis severity factor R_0. The severity factor (Abatzoglou et al., 1992) is defined as:

$$R_0 = \int_0^t e^{(T_\theta - T_{r\theta})/\omega} dt \qquad (8.1)$$

where: T_θ is the biomass processing temperature in °C, t is the time in min, $T_{r\theta}$ is the reference temperature in °C, and ω an empirical parameter (expressed in K to keep the exponent in dimensionless form) related with the activation energy, which can be expressed as:

$$\omega = \left(R \cdot T_r^2\right) / E \qquad (8.2)$$

where: R = 0.0083 kJ mol^{-1} K^{-1} and E is the activation energy (kJ mol^{-1}). In this work, treatments were carried up to reach maximum temperatures in the range 160–240°C. Assuming $T_{r\theta}$ = 100°C or T_r = 373 K and E = 104.0 kJ mol^{-1}, eq. (8.2) gives ω = 11.10 K; integration of eq. (8.1) allowed the calculation of R_0 for each experiment. The E value was estimated equal to 104.0 kJ mol^{-1}, as reported by Sidiras et al. (2011b).

Wheat straw's modification by auto-hydrolysis was examined by F.A. Batzias, I.G. Konstantinou, N.L. Vallaj, D.K. Sidiras, (2010), in the study "Diminishing an oil-products spill in seawater by using modified lignocellulosic residues as low cost adsorbents", which was presented in the 19th International Congress of Chemical and Process Engineering CHISA 2010, held in Prague.

The experimental reaction temperature profiles as a function of auto-hydrolysis time are presented in Fig. 8.6.

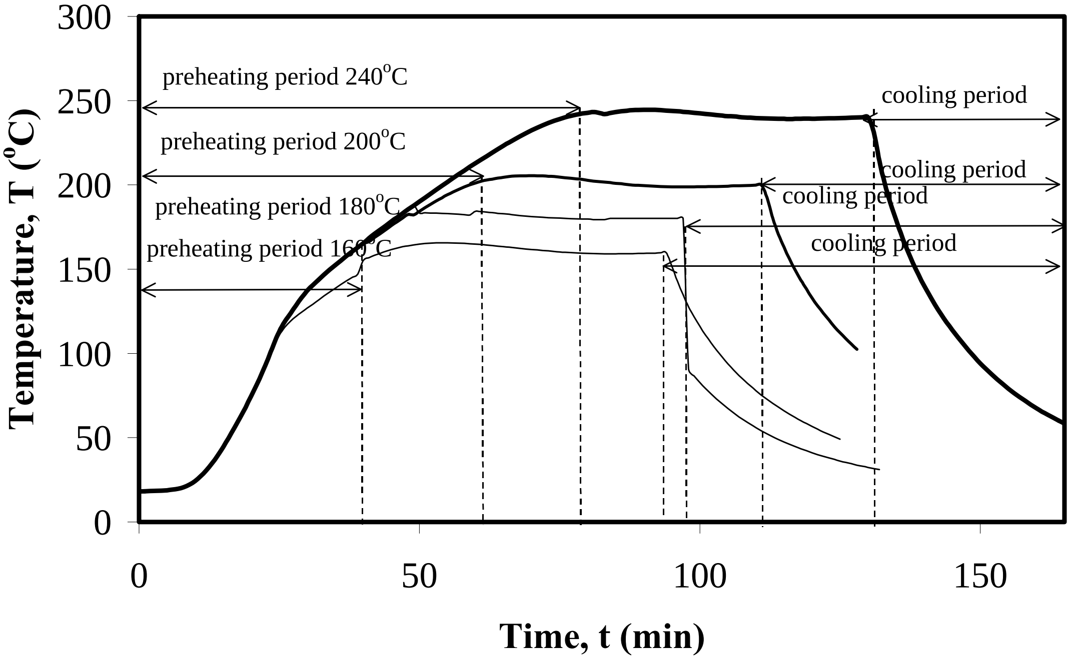


Fig. 8.6 Wheat straw's auto-hydrolysis temperature profile

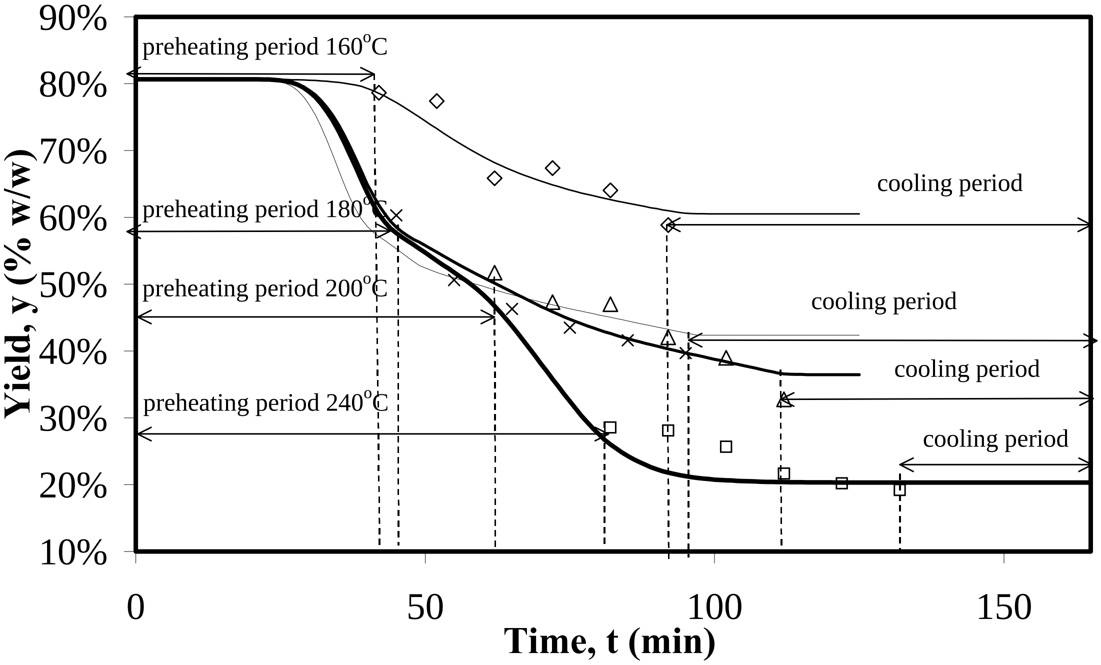


Fig. 8.7 Wheat straw auto-hydrolysis solid-residue yield vs. reaction time. The theoretical curves' values were simulated according to the model described by Batzias et al., (2010)

The wheat straw auto-hydrolysis solid-residue yield vs. reaction time is presented in Fig. 8.7.

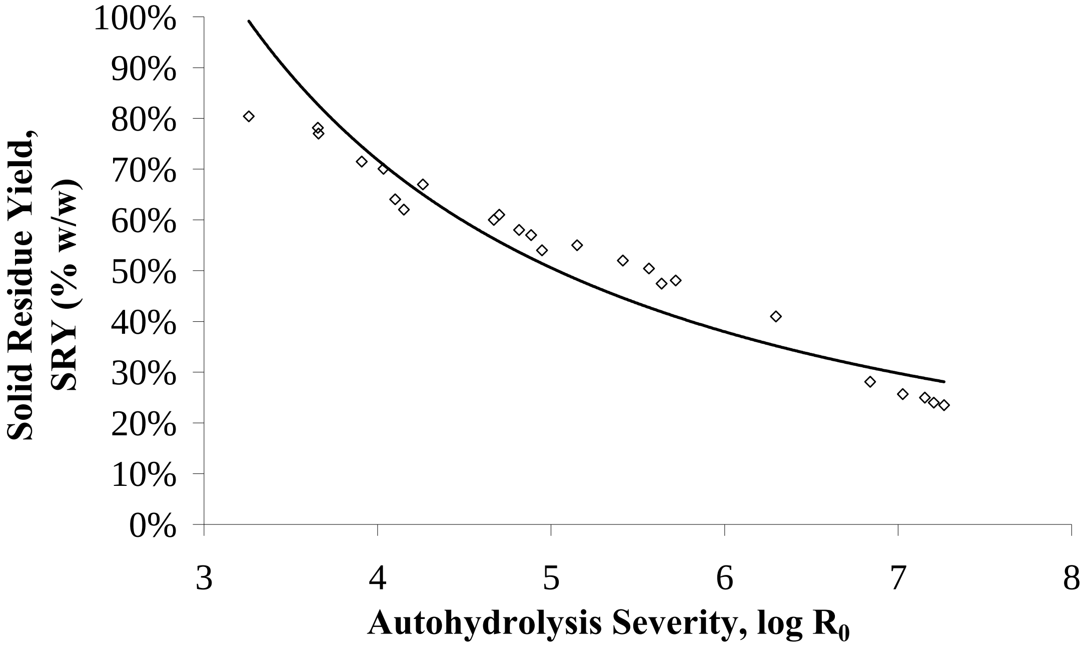


Fig. 8.8 SRY vs. Auto-hydrolysis Severity Factor for Wheat Straw treatment

As regards Auto-hydrolyzed Wheat Straw (AWS), for the optimal conditions of Diesel oil and Crude oil Adsorbencies ($\log R_0 = 5.0$, i.e., 180°C for 50 min), the Solid Residue Yield (SRY) was about 54% (Fig. 8.8).

8.4 Acid hydrolysis of wheat straw

Wheat straw's modification by acid hydrolysis was examined by D.K. Sidiras, and I.G. Konstantinou (2012b), in the study "Modification of barley straw by acid hydrolysis to be used as diesel and crude adsorbent", which was presented in the 5th WSEAS International Conference on Environmental and Geological Science and Engineering 2012, held in Vienna.

The experimental reaction temperature profiles as a function of acid hydrolysis time are presented in Fig. 8.9. The acid hydrolysis solid residue yield of the wheat straw (dry weight of product % w/w of the original dry material) is presented in Fig. 8.10 as a function of reaction time.

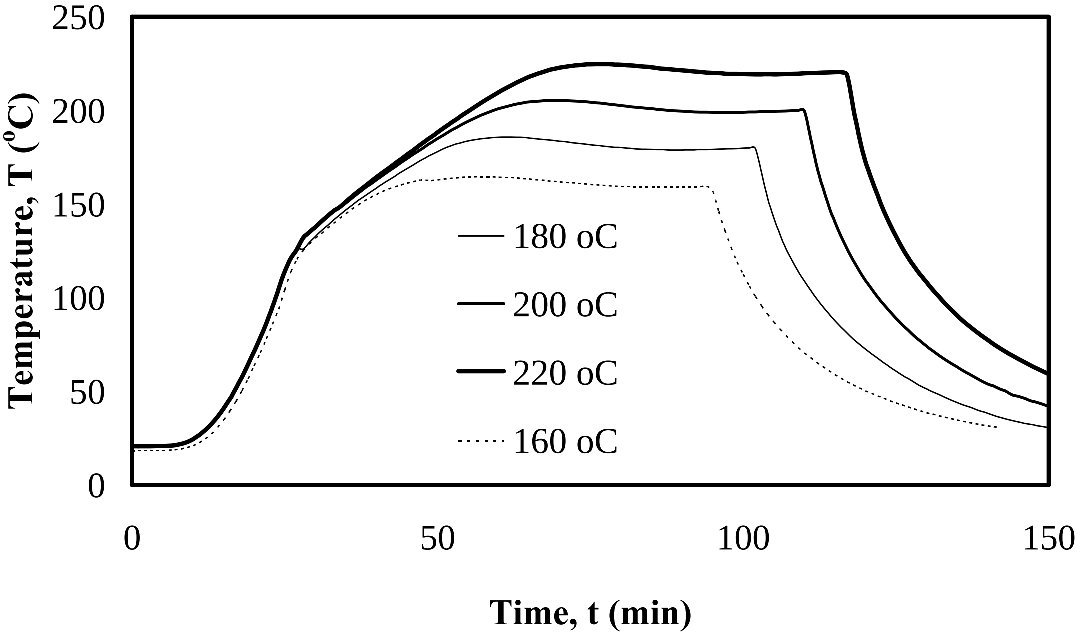


Fig. 8.9 Wheat straw’s acid hydrolysis temperature profile

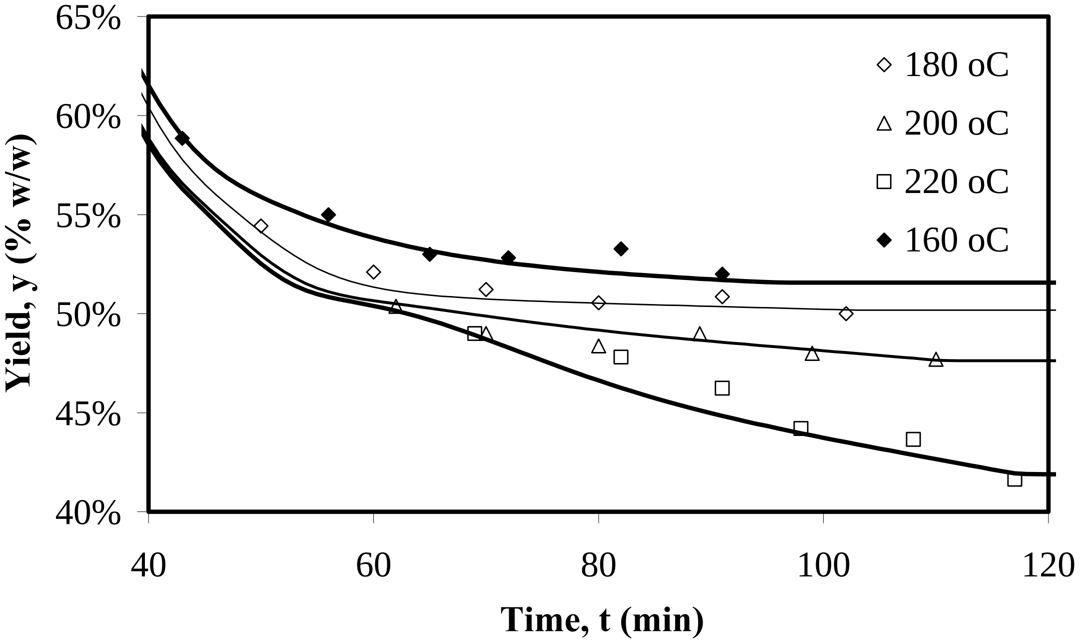


Fig. 8.10 Wheat straw acid hydrolysis solid-residue yield vs. reaction time. The theoretical curves’ values were simulated according to the model described by Sidiras, (2011); sulfuric acid concentration 0.045 N; liquid: solid ratio = 20:1

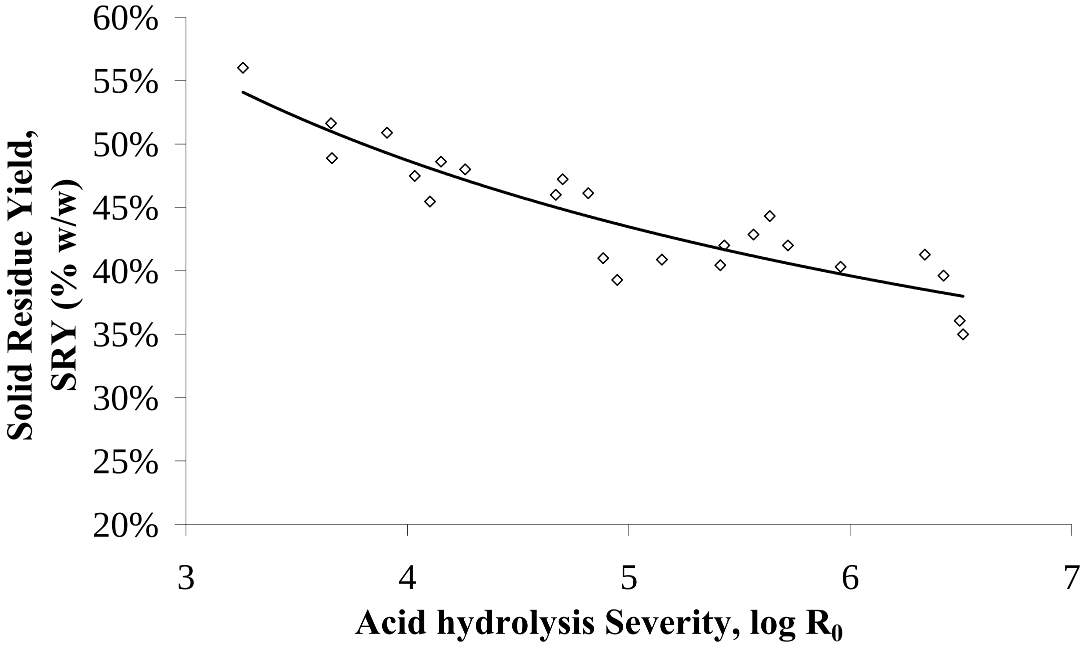


Fig. 8.11 SRY vs. Acid hydrolysis Severity Factor for Wheat Straw treatment

As regards Acid-hydrolyzed Wheat Straw (AcWS), for the optimal conditions of Diesel oil and Crude oil Adsorbencies ($\log R_0$ = 4.3-4.7, i.e., 180°C for 10-20 min, treated with 0.045 N H_2SO_4), the SRY was about 46-48% (Fig. 8.11). In the case of Auto-hydrolysis removal of 46% gave material of maximum oil (diesel oil and crude oil) adsorbencies, while in the case of Acid hydrolysis removal of 53% was needed.

8.5 Auto-hydrolysis of barley straw

Barley straw's modification by auto-hydrolysis was examined by D.K. Sidiras, I.G. Konstantinou, T.K. Politi, (2011c) in the study "Auto-hydrolysis modified barley straw as low cost adsorbent for oil spill cleaning", which was presented in the 19th European Biomass Conference and Exhibition 2011, held in Berlin.

The auto-hydrolysis temperature profile is shown in Fig. 8.12. The auto-hydrolysis process solid residue yield (SRY or y) of the barley straw (dry weight of product % w/w of the original dry material) is presented in Fig. 8.13 as a function of reaction time.

As regards Autohydrolyzed Barley Straw (ABS), for the optimal conditions of Diesel oil and Crude oil Adsorbencies ($\log R_0$= 5.0), the SRY was more than 51% (Fig. 8.14).

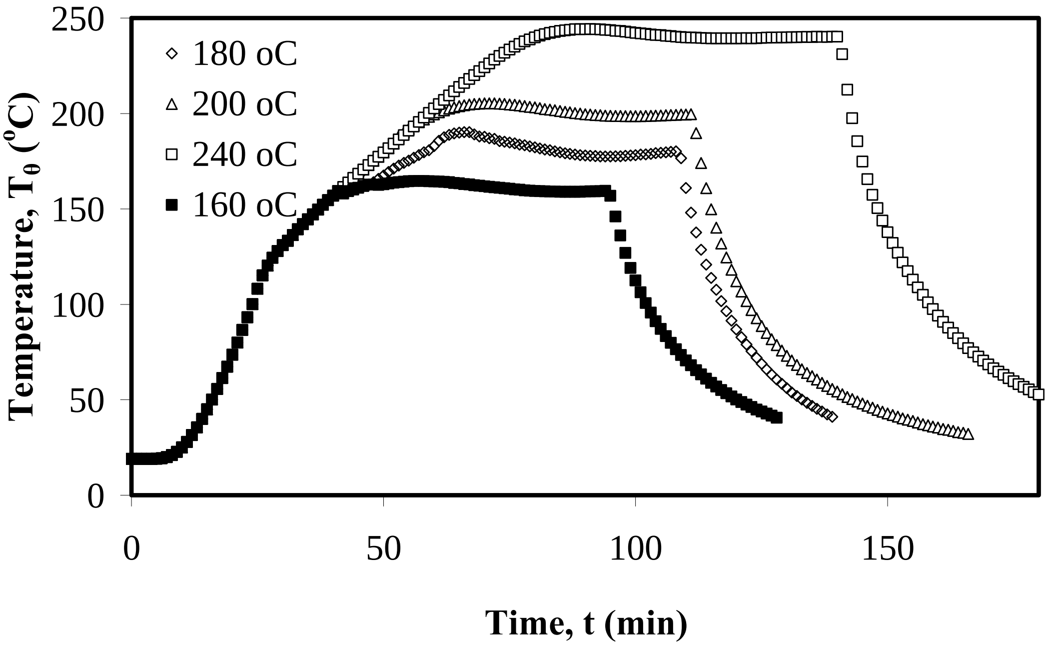


Fig. 8.12 Barley straw's auto-hydrolysis temperature profile

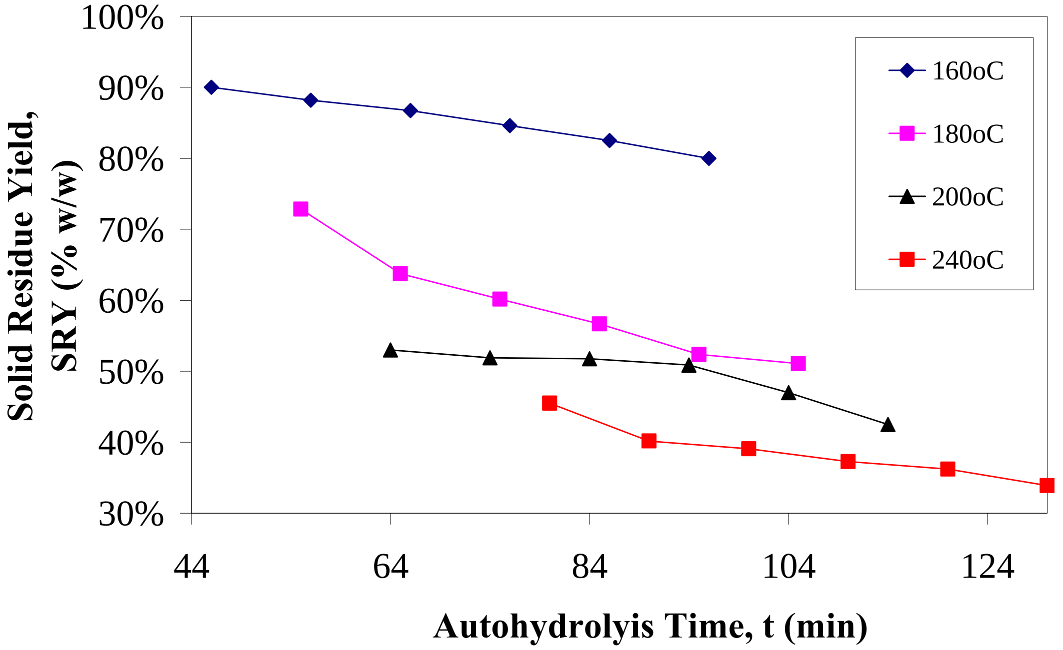


Fig. 8.13 Barley straw auto-hydrolysis solid-residue yield (SRY) vs. reaction time

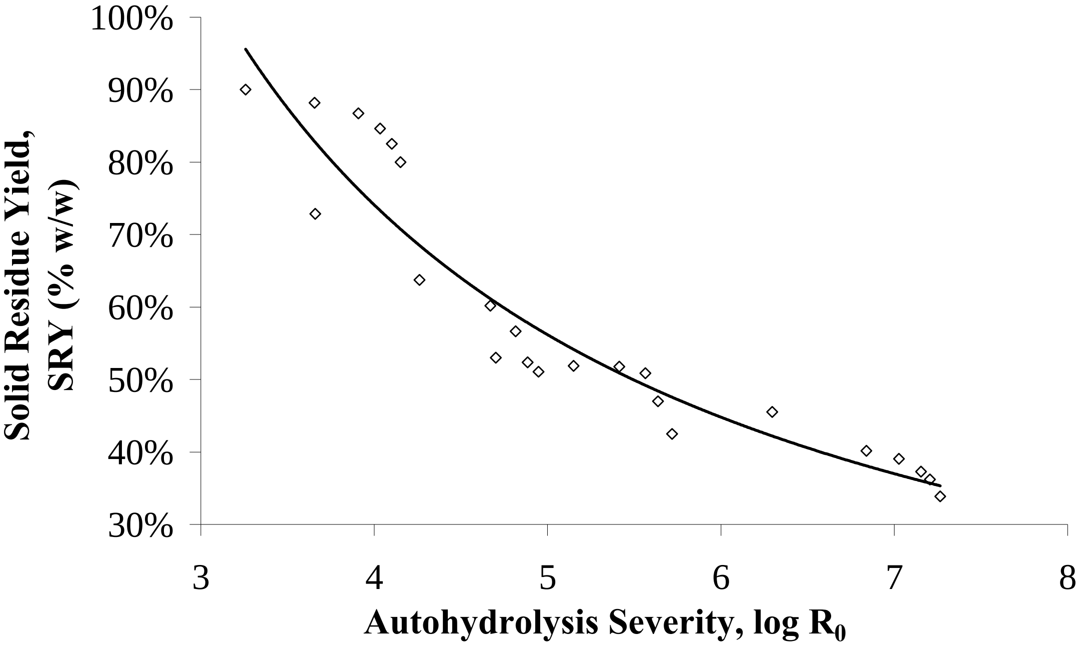


Fig. 8.14 SRY vs. Auto-hydrolysis Severity Factor for Barley Straw treatment

8.6 Acid hydrolysis of barley straw

Barley straw's modification by acid hydrolysis was examined by D.K. Sidiras, and I.G. Konstantinou (2012a), in the study "A new oil spill adsorbent from sulfuric acid modified wheat straw", which was presented in the 20th European Biomass Conference and Exhibition 2012, held in Milan.

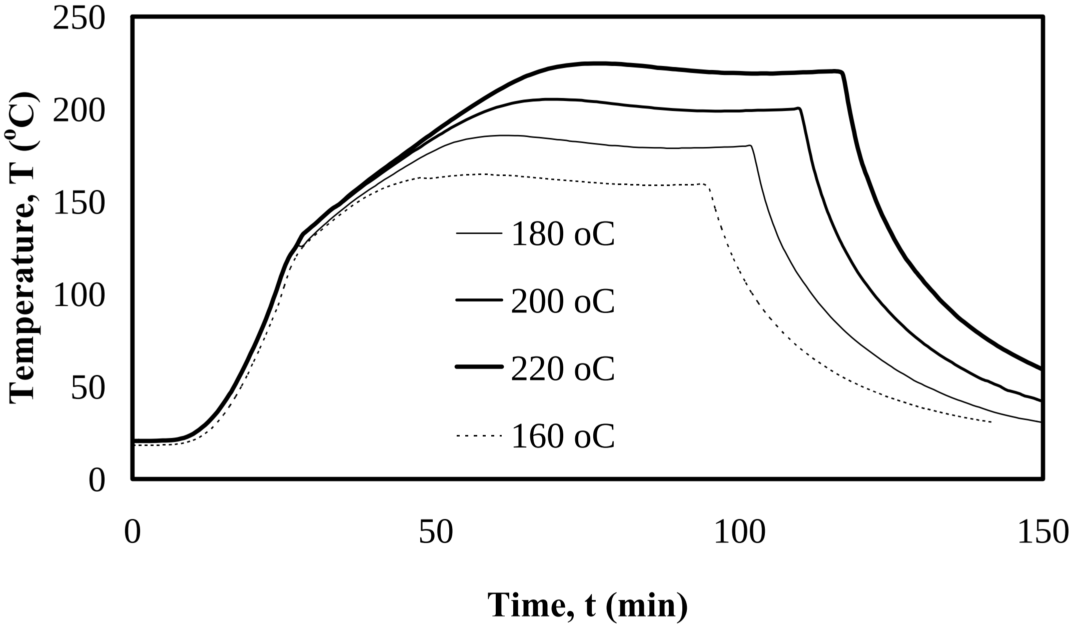


Fig. 8.15 Barley straw's acid hydrolysis temperature profile

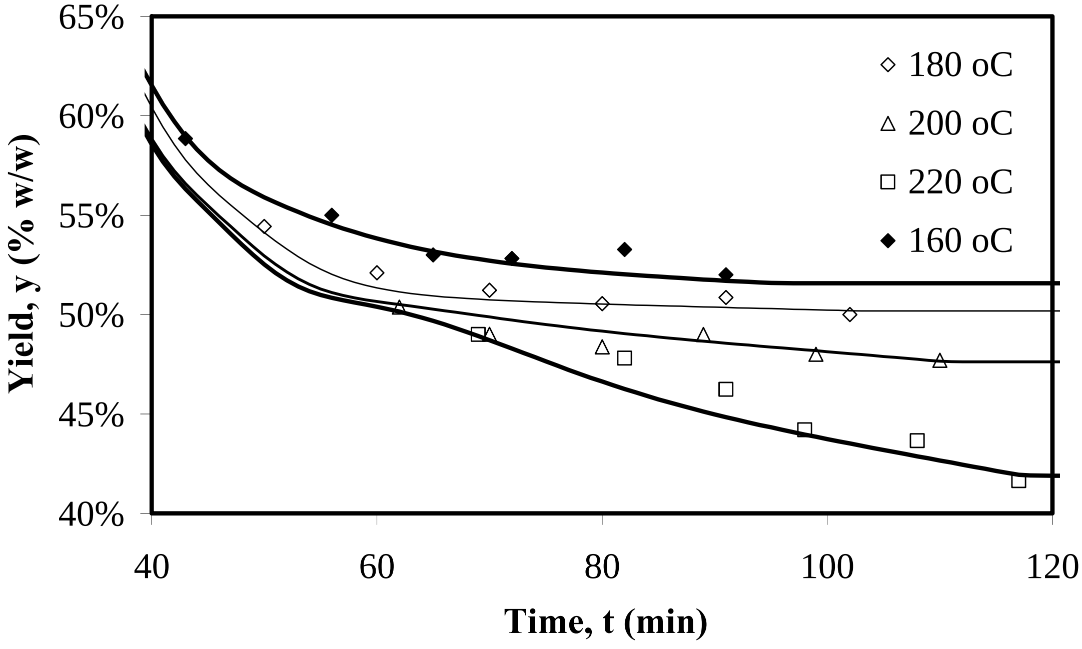


Fig. 8.16 Barley straw acid hydrolysis solid-residue yield vs. reaction time. The theoretical curves’ values were simulated according to the model described by Sidiras, (2011); sulfuric acid concentration 0.045 N; liquid: solid ratio = 20:1

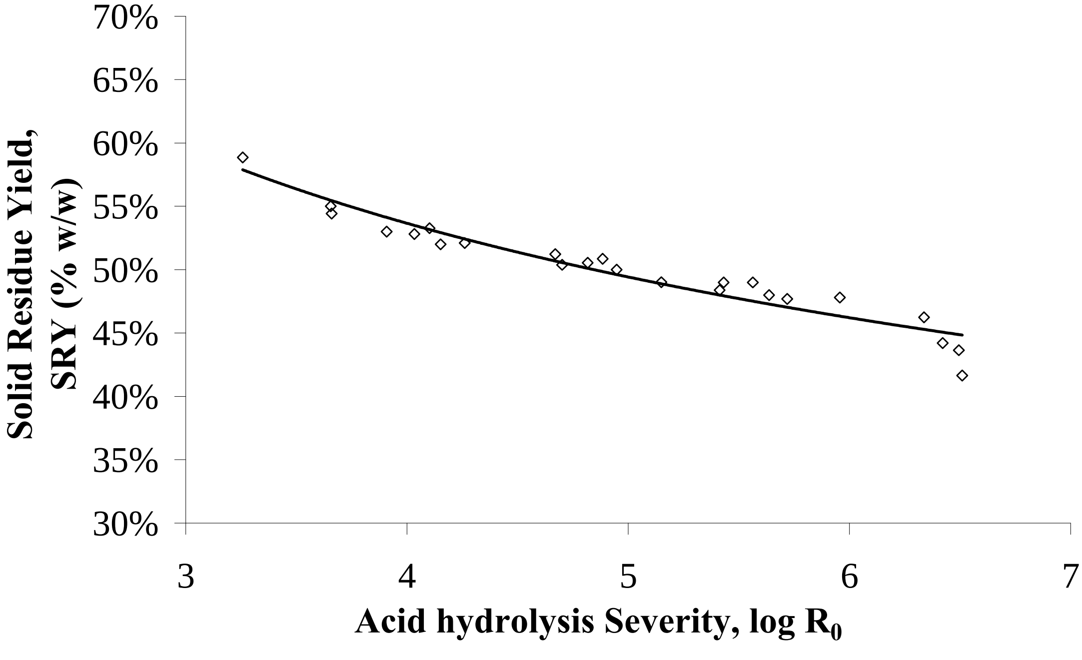


Fig. 8.17 SRY vs. Acid hydrolysis Severity Factor for Barley Straw treatment

The acid hydrolysis temperature profile is shown in Fig. 8.15. The acid hydrolysis solid-residue yield is presented in Fig. 8.16, as a function of reaction time. As regards Acid-hydrolyzed Barley Straw (AcBS), for the optimal conditions Crude oil Adsorbency ($\log R_0$ = 4.3), the SRY was 52% (Fig. 8.17). Auto-hydrolysis and Acid hydrolysis of Barley Straw gave maximum oil (diesel oil and crude oil) adsorbencies, for 48% material removal (1-SRY = 48%). The appropriate conditions are 180^{o}C for 50 min for Auto-hydrolysis and 180^{o}C for 10 min, treated with 0.045 N H_2SO_4, for Acid hydrolysis treatment.

8.7 Wheat – barley straw autohydrolyzed – acid hydrolyzed comparisons

In this sub-chapter auto-hydrolyzed SRY values compared to those of acid hydrolyzed for both wheat and barley straw. More specific, in Fig. 8.18 AWS SRY values compared to those of AcWS SRY values, in Fig. 8.19 ABS SRY values compared to those of AcBS SRY values, while in Figs 8.20 and 8.21 AWS SRY values compared to ABS SRY values and AcWS SRY values compared to AcBS SRY values, respectively.

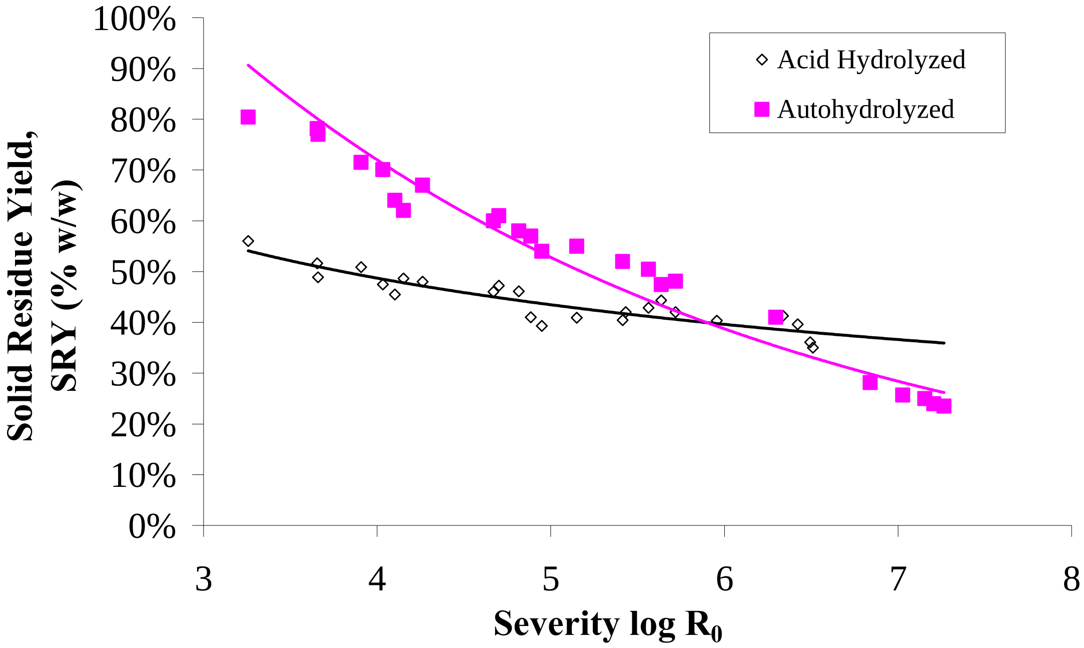


Fig. 8.18 SRY vs. Severity Factor R_0 for AWS and AcWS

Auto-hydrolysis SRY values are in general higher than those of Acid hydrolysis for both wheat and barley straw (Figs 8.18, 8.19), i.e., the use of sulfuric acid results to lower SRY values in comparison with the case that no acid (or other chemical) was added.

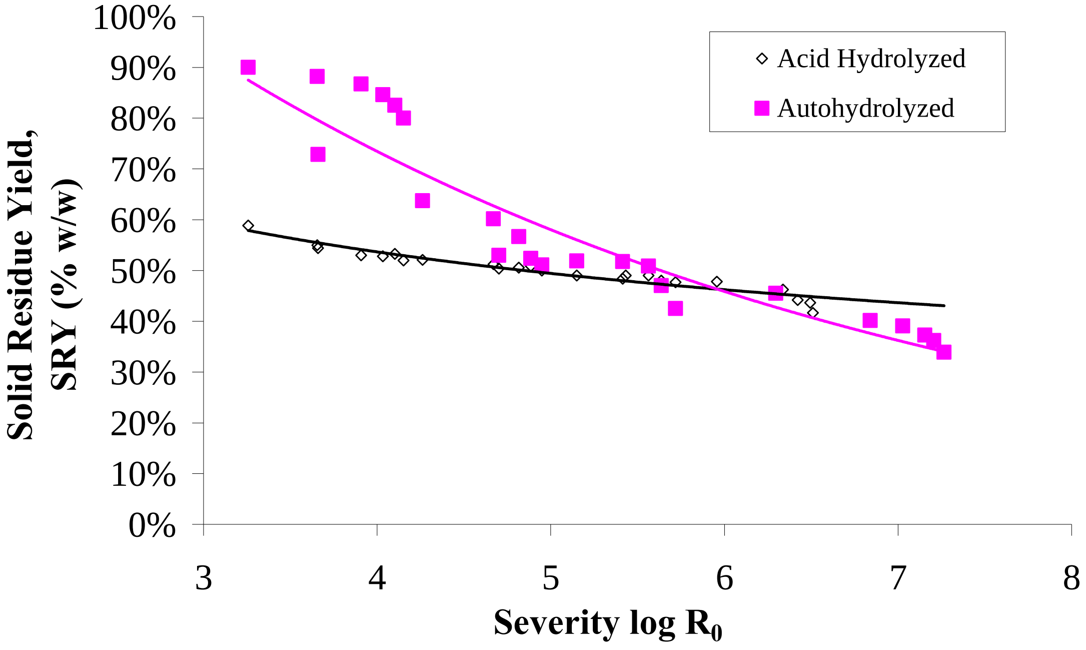


Fig. 8.19 SRY vs. Severity Factor R_0 for ABS and AcBS

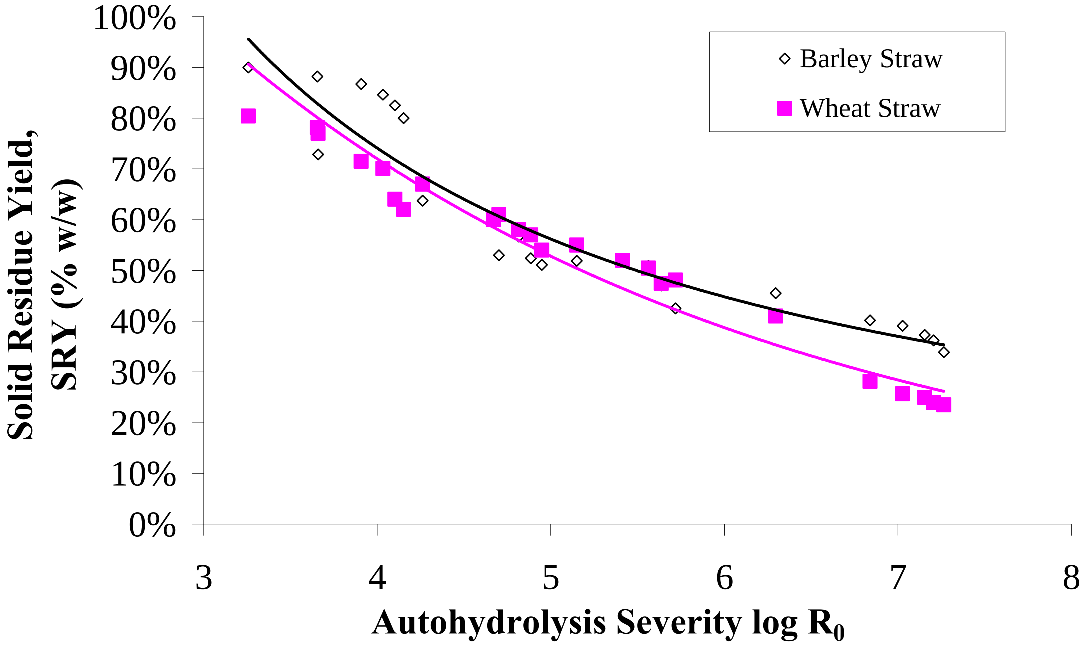


Fig. 8.20 SRY vs. Severity Factor R_0 for AWS and ABS

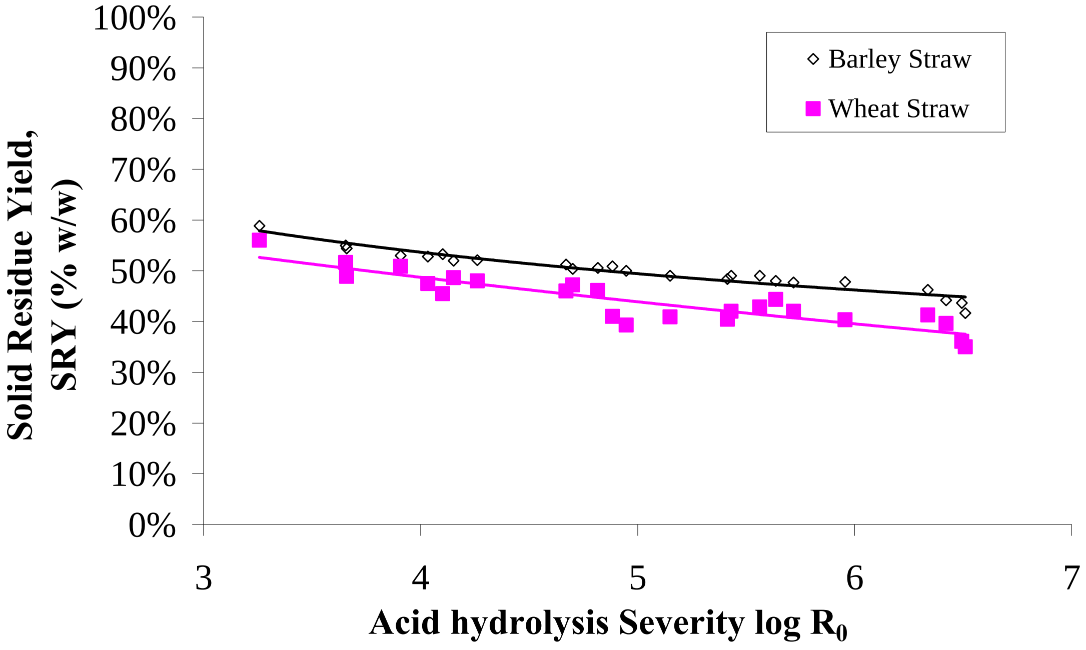


Fig. 8.21 SRY vs. Severity Factor R_0 for AcWS and AcBS

SRY values of AWS were slightly lower than those of ABS for the same Severity Factor (Fig. 8.20). SRY values of AcWS were lower than those of AcBS for the same Severity Factor (Fig. 8.21).

CHAPTER 9
ADSORBENCY RESULTS AND DISCUSSION

9.1 Introduction

From the materials that were available to be modified in the autoclave, (pine sawdust, spruce sawdust, wheat straw and barley straw), straw (wheat and barley) was selected to be experimentally measured for its adsorption capacities, due to its ability to float in an aquatic environment. This ability is mainly due to the structure and the grain size of as obtained after thermal processing of hydrolysis (autohydrolysis and acid hydrolysis). Straw is a renewable material for the production of cellulose, glucose and other chemical compounds.

The waxy surface of the straw makes it able to absorb hydrophobic liquids. Studies have shown that microorganisms degrade hydrocarbons are present in all aquatic ecosystems, and where there are abundant oil. Therefore, microorganisms that grow on the surface of straw can produce enzymes to break down oily. This selection is an important advantage of straw as adsorbent material for purification of wastewater containing hydrocarbons.

The surface properties of straw play a crucial role. A thin wax layer covering stalks and leaves of cereals is composed of esters, long chain fatty acids and monohydroxy alcohols, therefore straw should favorably adsorb hydrophobic liquids. Wax coverage making the straw surface hydrophobic, as well as capillary forces, determines the efficiency of oil removal (Wisniewska et al., 2003).

The adsorption capacity depends primarily on the chemical structure of straw tissue that has direct contact with oil. Oil is mostly held due to capillary of straw tissue and interior part of stalk, as well as to the existence of oil bridges between stalks. Straw adsorption capacity varies for many researches due to straw surface properties, different apparent densities and ways of its adsorbent form (Witka-Jezewska et al., 2003).

Two methods are simple and inexpensive in order to put out the used adsorbent from the open sea in real oil spill conditions: magnetically modification of the adsorbent (wheat straw) after its contact with water-based magnetic fluid (Safarik et al., 2005). Moreover, straw can be applied enclosed or pressed to a mat-form (Suni et al., 2004).

9.2 Model

The theoretical adsorbency values A_{ijk} curve is estimated by the solution of the following expressions, suggested in the present work:

$$dA'_{ijk} / dR_0 = b_{1ijk} \cdot (A'_{\infty,ijk} - A'_{ijk}) \tag{9.1}$$

$$dA_{ijk} / dR_0 = b_{1ijk} \cdot (A'_{\infty,ijk} - A'_{ijk}) - b_{2ijk} \cdot A_{ijk} \tag{9.2}$$

where: b_{1ijk} and b_{2ijk} are empirical constants. The subscripts takes the values $i=W, D, C$, $j=P, D, C$ and $k=N, F, S$ (W stands for water, D for diesel, C for crude oil, P for pure, N for 'not oil spill', F for freshwater and S for seawater). The variable A'_{ijk} is the adsorbency potential, which is an increasing function of R_0, that is a measure of process intensification. The parameter $A'_{\infty,ijk}$ is the asymptote of A'_{ijk} for $R_0 \rightarrow \infty$. The differential eq. (9.1) represents the increasing trend of the adsorbency due to the increasing of the lignin content, the BET specific surface, and the surface roughness of the AWS. Differential eq. (9.3) incorporates the decreasing trend of the adsorbency due to the distraction of the structure of the AWS, the removal of natural waxes and the precipitation of auto-hydrolysis decomposition products (from furfural and 5-hydroxymethylfurfural decomposition) on this adsorbent. Eq. (9.3) is the analytical solution of above differential equation system:

$$A_{ijk} = (A'_{\infty,ijk} - A_{0,ijk}) b_{1ijk} / (b_{2ijk} - b_{1ijk}) \left(e^{-b_{1ijk} \cdot R_0} - e^{-b_{2ijk} \cdot R_0} \right) + A_{0,ijk} e^{-b_{2ijk} \cdot R_0} \tag{9.3}$$

where: the constant $A_{0,ijk}$ is the value of A_{ijk} for $R_0=0$, i.e., for the untreated lignocellulosic material.

9.3 Autohydrolyzed wheat straw adsorbencies

Pure liquids

Auto-hydrolyzed wheat straw's adsorbency in the case of pure liquids was examined by F.A. Batzias, I.G. Konstantinou, N.L. Vallaj, D.K. Sidiras, (2010), in the study "Diminishing an oil-products spill in seawater by using modified lignocellulosic residues as low cost adsorbents", which was presented in the 19th International Congress of Chemical and Process Engineering CHISA 2010, held in Prague. The experimental results of the water and oil (diesel oil/ crude oil) adsorbency of the untreated (UWS) and the auto-hydrolyzed wheat straw (AWS) are shown in the following diagrams.

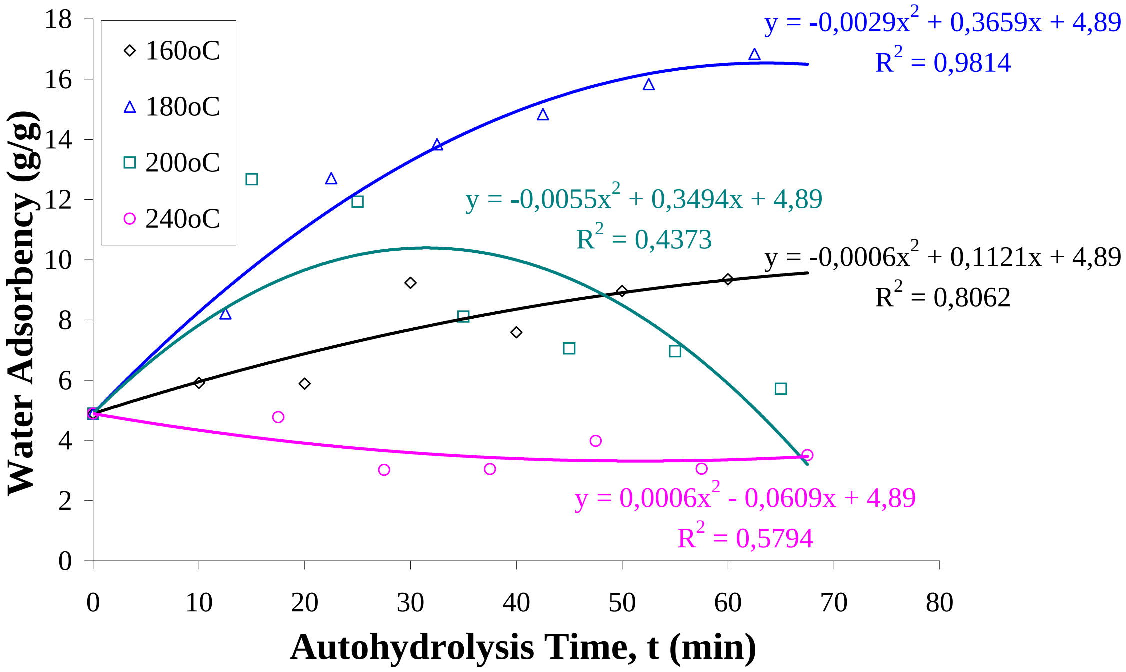


Fig. 9.1 UWS and AWS water adsorbency values vs. the auto-hydrolysis time

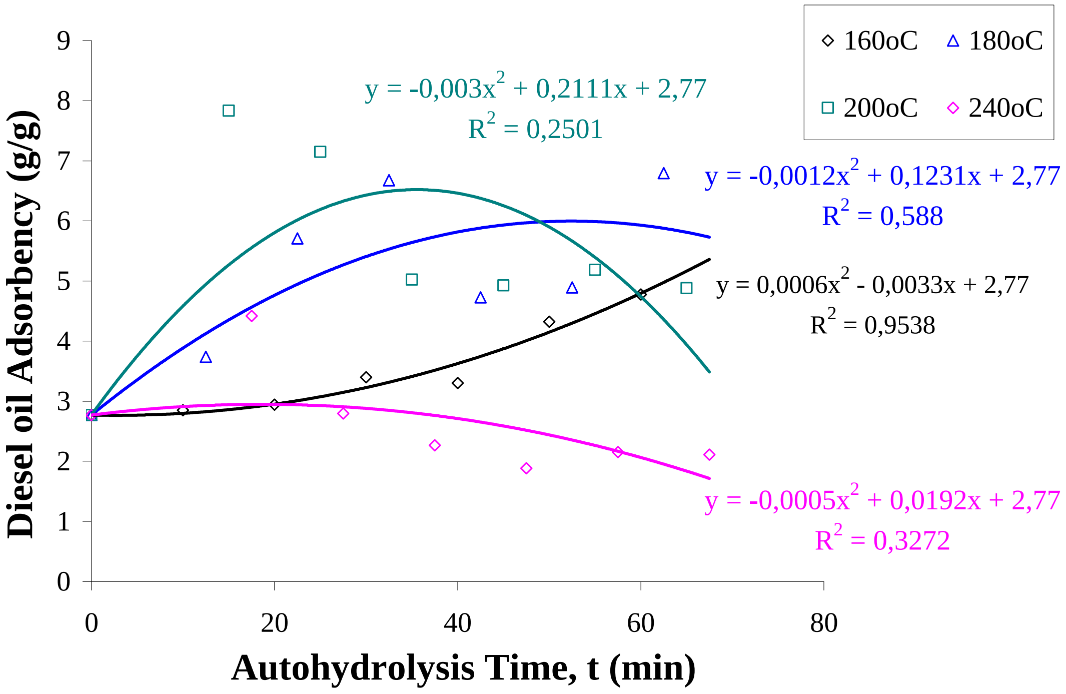


Fig. 9.2 UWS and AWS diesel oil adsorbency values vs. the auto-hydrolysis time

In Figure 9.1, the water adsorbency vs. the auto-hydrolysis time for reaction-ending temperatures of 160, 180, 200 and 240°C, showed an increasing trend as a function of the auto-hydrolysis time in the cases of 160 and 180°C, whereas the trend was decreasing at 240°C. The water adsorbency at reaction-ending temperature of 200°C was increasing for auto-hydrolysis time less than 30 min and then decreased; the maximum of water adsorbency was about 10 g/g.

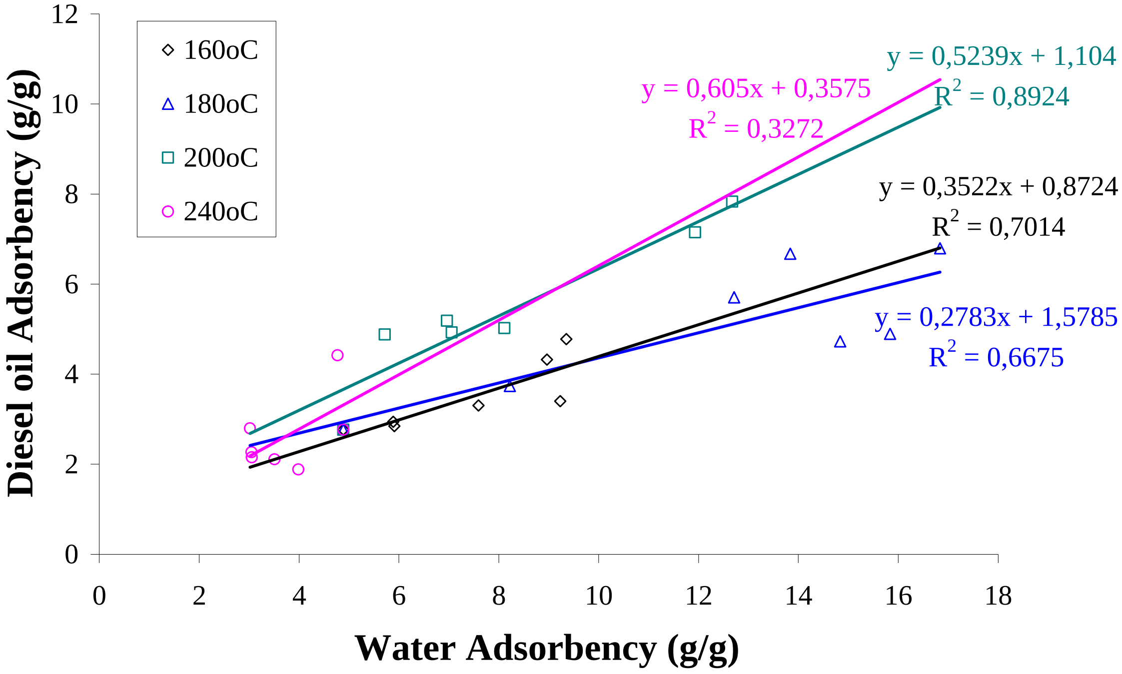


Fig. 9.3 UWS and AWS diesel oil adsorbency values vs. water adsorbency values

According to the Figure's 9.2 data, diesel oil adsorbency as a function of the auto-hydrolysis time showed an increasing trend for reaction-ending temperatures 160 and 180°C, whereas the trend was decreasing at 240°C. The diesel oil adsorbency at reaction-ending temperature of 200°C was increasing for auto-hydrolysis time less than 35 min and then was decreasing; the maximum of diesel oil adsorbency was about 7 g/g. The diesel oil adsorbency shows a good linear correlation vs. the water adsorbency for all auto-hydrolysis reaction-ending temperatures (Fig. 9.3).

This adsorbency increasing-rate was higher for 200 and 240°C auto-hydrolysis reaction-ending temperatures, when compared with the rates for 160 and 180°C. As it can be seen in Figure 9.4, diesel oil adsorbency % increase was higher than water adsorbency % increase for 200°C auto-hydrolysis reaction-ending temperature.

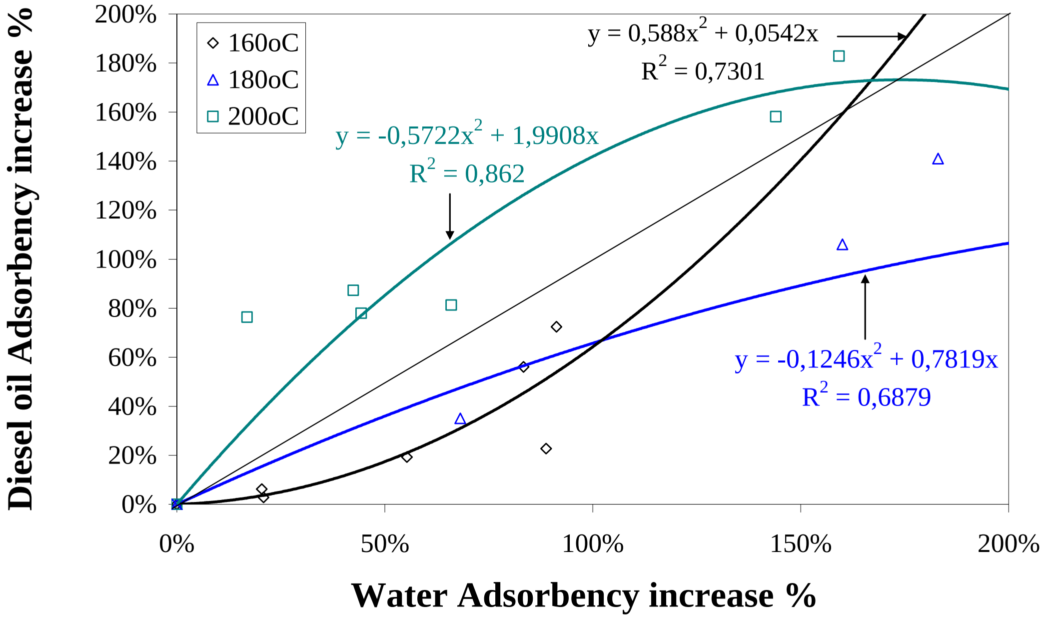


Fig. 9.4 Diesel oil adsorbency % increase vs. water adsorbency % increase

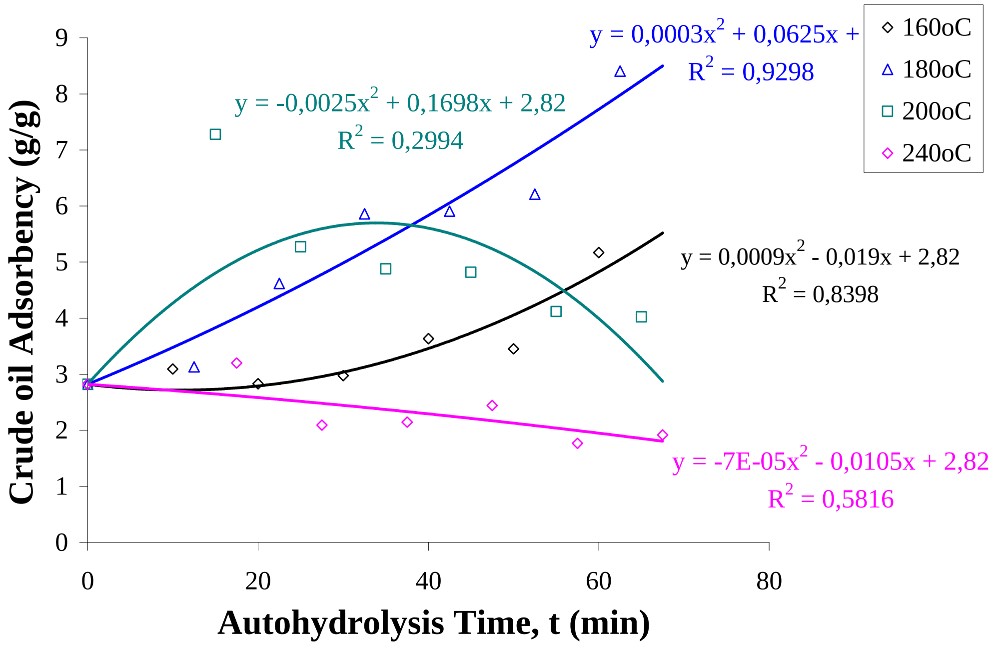


Fig. 9.5 UWS and AWS crude oil adsorbency values vs. the auto-hydrolysis time

According to the Figure’s 9.5 data, crude oil adsorbency as a function of the auto-hydrolysis time was increasing for reaction-ending temperatures 160, and 180°C and decreasing for 240°C. Crude oil adsorbency was increasing for auto-hydrolysis time less than 35 min for reaction-ending temperatures 200°C, and then was decreasing. The maximum of crude oil adsorbency was about 6 g/g.

This adsorbency shows a significant linear correlation vs. the water adsorbency for auto-hydrolysis reaction-ending temperatures 160-240°C (Fig. 9.6). The adsorbency increasing-rate was higher for auto-hydrolysis reaction-ending temperatures 200 and 240°C compared with the rates at 160 and 180°C.

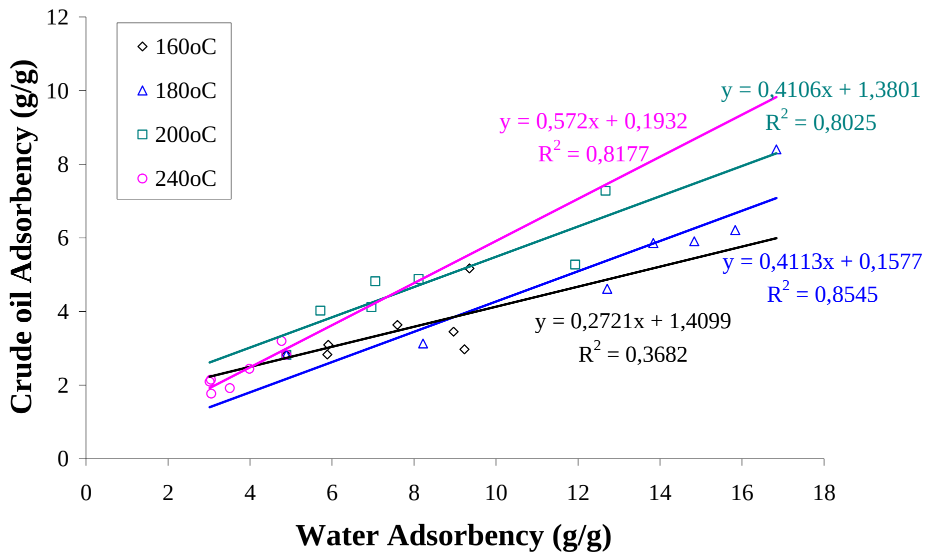


Fig. 9.6 UWS and AWS crude oil adsorbency values vs. water adsorbency values

As it can be seen in Figure 9.7, crude oil adsorbency % increase was higher than water adsorbency % increase for auto-hydrolysis reaction-ending temperature 200°C.

The water adsorbency is presented in Figure 9.8 vs. solid residue yield (SRY), for auto-hydrolysis reaction-ending temperatures range from 160 to 240°C; it is worthwhile noting that maximum water adsorbency is observed for SRY approximately 40-50%.

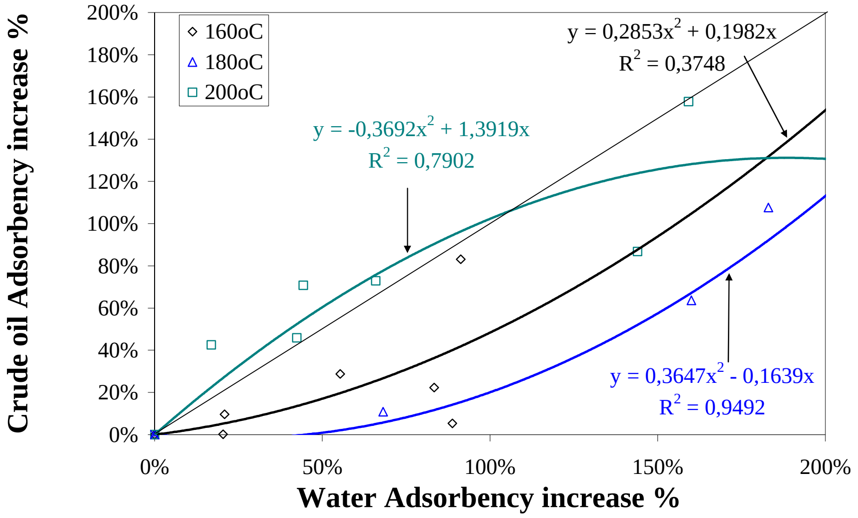


Fig. 9.7 Crude oil adsorbency % increase vs. water adsorbency % increase

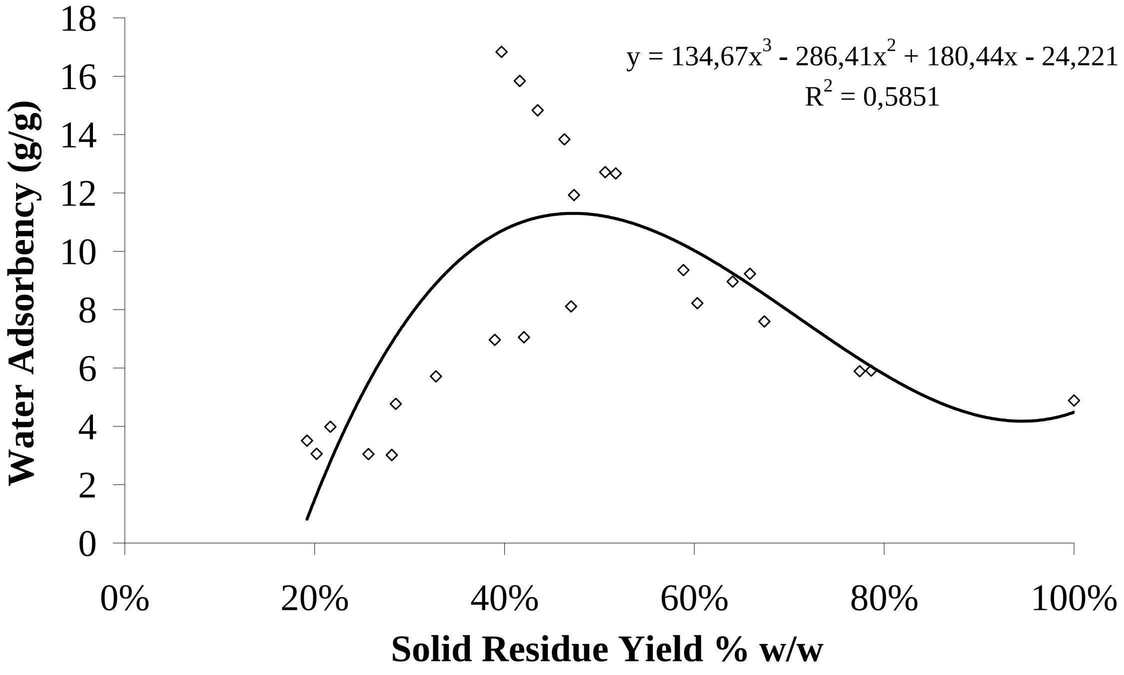


Fig. 9.8 Water adsorbency values vs. SRY, for temperatures ranging from 160-240^{o}C

Figure 9.9 presents the diesel oil adsorbency vs. SRY, for auto-hydrolysis reaction-ending temperatures range from 160 to 240^{o}C. Once again maximum diesel oil adsorbency value is observed for SRY of approximately 45%. Figure 9.10 presents the crude oil adsorbency vs. SRY, for auto-hydrolysis reaction-ending temperatures range from 160 to 240^{o}C. There is, also, a maximum value of crude oil adsorbency for SRY of approximately 45%.

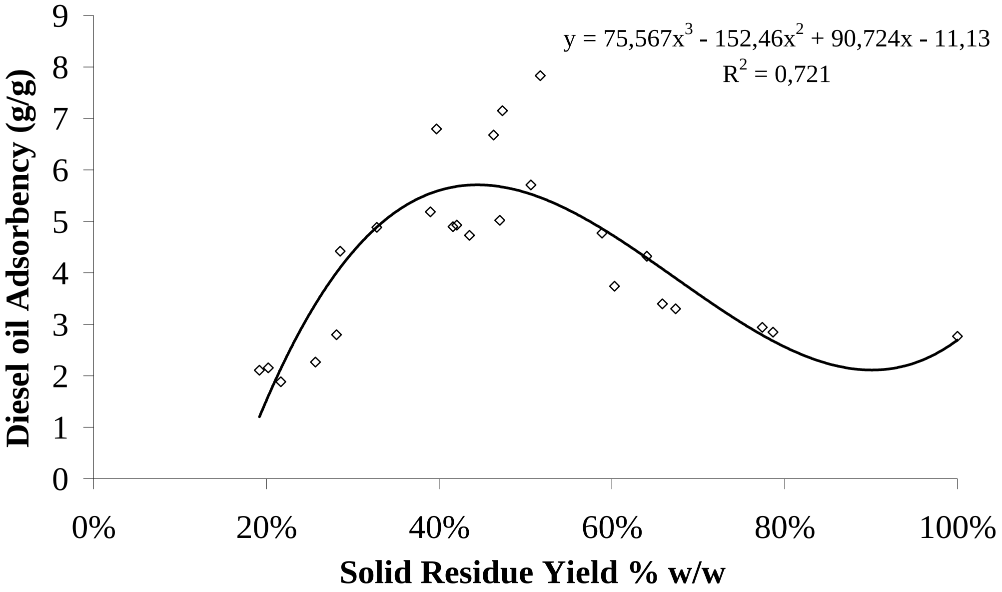


Fig. 9.9 Diesel oil adsorbency values vs. SRY, for temp. ranging from 160-240^{o}C

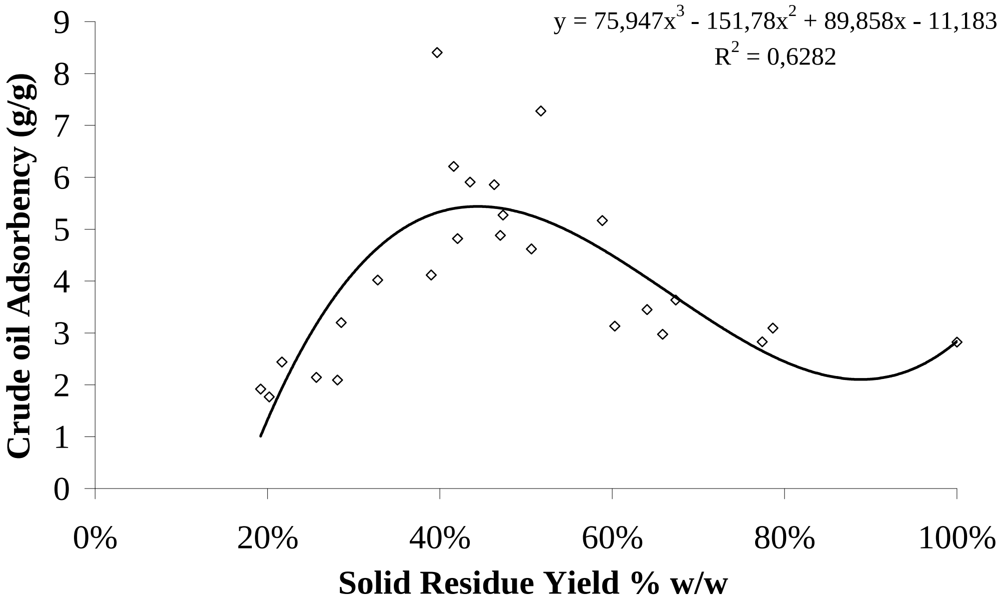


Fig. 9.10 Crude oil adsorbency vs. SRY, for temperatures ranging from 160-240^{o}C

In Figure 9.11, (a) diesel oil adsorbency vs. water adsorbency, (b) crude oil adsorbency vs. water adsorbency, and (c) diesel oil adsorbency vs. crude oil adsorbency, are given for the auto-hydrolysis reaction-ending temperatures range from 160 to 240^{o}C. The linear correlation coefficients were relatively high indicating linear correlation between these adsorbency-values.

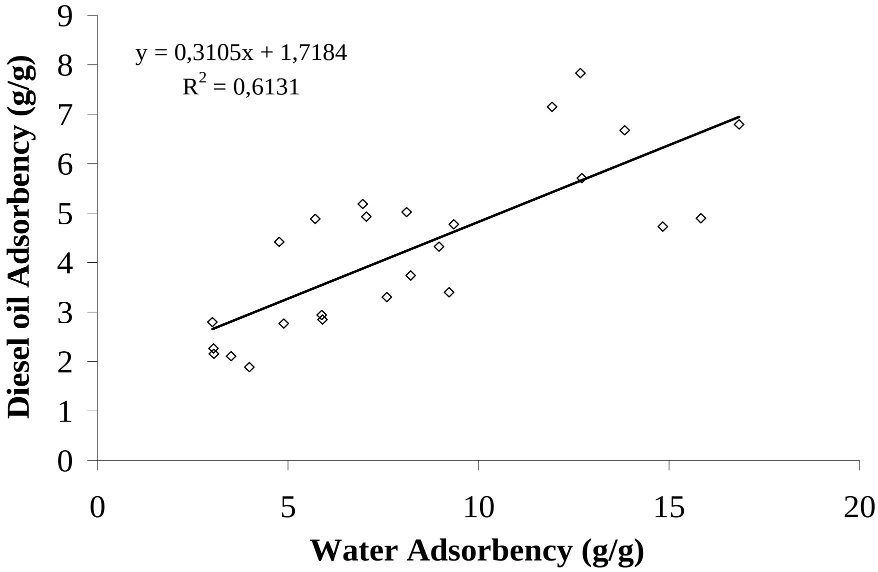


Fig. 9.11a Diesel oil adsorbency values vs. water adsorbency values

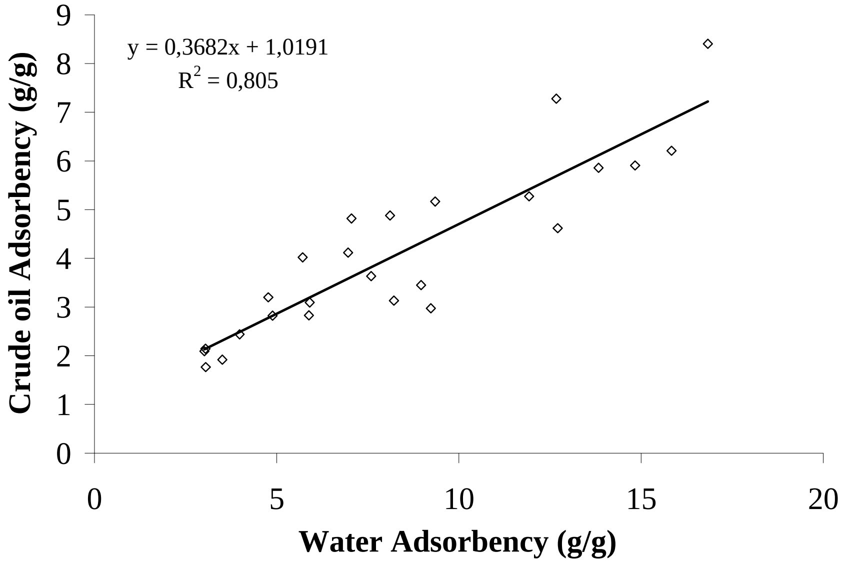


Fig. 9.11b Crude oil adsorbency values vs. water adsorbency values

Water, diesel and crude oil adsorbency of untreated and modified wheat straw in the case of pure liquids are given in Table 9.1. In Fig. 9.12, the water adsorbency A_{WPN}, in the case of pure water (not oil spill), is presented as a function of the auto-hydrolysis severity factor R_0. For better presentation this factor is shown in its in logarithmic version log R_0.

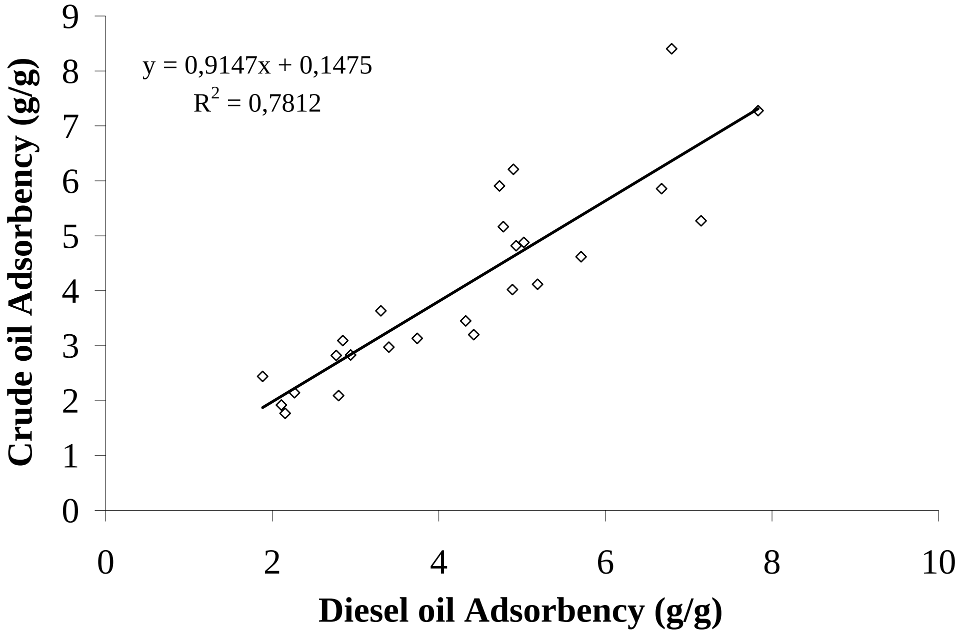


Fig. 9.11c Diesel oil adsorbency values vs. crude oil adsorbency values

The range of auto-hydrolysis ending temperatures is 160-240^{o}C. In this case $i=W$, $j=P$, $k=N$. The experimental water adsorbency-values are shown to increase up to a maximum of 13.84 g/g for log R_0=4.67, i.e., by intensifying the auto-hydrolysis isothermal time to 20 min (not including preheating period) and temperature to 180^{o}C.

According to the proposed novel model, the theoretical water adsorbency-values increase up to a maximum of 13.07 g/g for log R_0=4.70, i.e., by intensifying the auto-hydrolysis temperature to 200^{o}C for isothermal time 0 min (when the reactor's temperature reaches the preset value of 200^{o}C, the cooling procedure starts immediately).

In Fig. 9.13, the diesel adsorbency A_{DPN}, in the case of pure diesel (not oil spill), is presented as function of log R_0. The theoretical adsorbency values curve is estimated by eq. (8.2) for $i=D$, $j=P$ and $k=N$. The experimental A_{DPN} values are shown to increase up to a maximum of 7.83 g/g for log R_0=4.70, i.e., by intensifying the auto-hydrolysis isothermal time to 0 min and temperature to 200°C. According to the proposed model, the theoretical values increase up to a maximum of 5.80 g/g for log R_0=4.95, i.e., by intensifying the auto-hydrolysis isothermal time to 50 min and temperature to 180°C.

Table 9.1 Water, diesel and crude oil adsorbency of untreated and auto-hydrolyzed wheat straw in the cases of pure liquids and oil spills on freshwater/seawater

T (°C)	t (min)	Pure			Diesel oil spill on freshwater		Crude oil spill on freshwater		Diesel oil spill on seawater		Crude oil spill on seawater	
		Water	Diesel oil	Crude oil	Water	Diesel oil	Water	Crude oil	Water	Diesel oil	Water	Crude oil
		Adsorbency (g/g)										
Untreated		4.89	2.77	2.82	1.68	3.17	1.29	4.36	0.88	2.76	0.94	4.08
160	0	5.91	2.85	3.09	1.21	4.05	0.75	4.01	2.03	3.93	1.53	4.03
160	10	5.89	2.94	2.83	1.07	3.46	0.99	4.44	2.84	4.35	1.45	3.98
160	20	9.23	3.40	2.97	0.95	3.89	1.34	2.83	2.85	4.13	1.03	3.29
160	30	7.59	3.30	3.63	1.64	4.51	1.19	3.74	2.87	3.91	1.62	4.25
160	40	8.96	4.32	3.45	1.50	4.88	1.56	3.43	3.16	3.94	0.74	5.21
160	50	9.35	4.77	5.17	1.75	5.41	2.09	4.39	3.16	5.27	1.17	4.72
180	0	8.22	3.74	3.13	1.01	3.87	0.98	4.76	2.85	4.24	1.06	3.88
180	10	12.71	5.71	4.62	3.25	6.22	0.81	5.11	3.45	5.00	0.61	4.65
180	20	13.84	6.67	5.86	3.11	5.43	3.59	7.08	3.60	4.73	0.71	4.58
180	30	13.00	4.73	5.91	1.47	6.00	2.39	9.04	2.13	5.27	1.60	4.71
180	40	13.00	4.90	6.21	1.69	7.30	1.75	9.08	2.07	6.26	1.83	5.07
180	50	13.03	6.80	8.40	3.60	7.15	2.13	8.72	2.12	5.71	1.55	6.22
200	0	12.67	7.83	7.28	3.31	5.83	1.20	7.24	3.49	5.23	2.03	6.48
200	10	11.93	7.15	5.27	1.18	6.13	2.82	8.36	2.72	6.65	1.76	6.91
200	20	8.11	5.02	4.88	1.19	5.94	0.92	7.70	1.76	5.77	1.75	4.85
200	30	7.06	4.93	4.82	0.80	5.69	0.56	7.04	1.34	4.89	1.98	4.47
200	40	6.96	5.19	4.12	1.23	5.45	1.55	6.45	1.46	4.51	1.17	5.41
200	50	5.72	4.88	4.02	0.80	5.03	0.84	6.11	1.47	4.62	1.72	4.61
240	0	4.77	4.42	3.20	0.55	4.94	0.75	5.14	0.80	4.22	0.73	4.01
240	10	3.02	2.80	2.09	1.07	3.68	0.49	3.58	0.58	2.63	0.90	3.40
240	20	3.05	2.27	2.14	0.84	3.47	1.30	3.60	0.56	2.94	1.04	3.89
240	30	3.99	1.89	2.44	0.77	2.96	0.41	2.96	0.86	1.35	0.19	2.66
240	40	3.06	2.16	1.77	0.00	2.45	0.37	2.25	0.66	1.44	0.52	2.31
240	50	3.51	2.11	1.92	0.28	2.44	0.18	2.82	0.83	1.65	0.17	2.76

In Fig. 9.14, the crude oil adsorbency A_{CPN}, in the case of pure crude oil (not oil spill), is presented as functions of log R_0. The theoretical adsorbency values curve is estimated by eq. (8.2) for $i=C$, $j=P$ and $k=N$.

The experimental A_{CPN} values are shown to increase up to a maximum of 8.40 g/g for log R_0=4.95, i.e., by intensifying the auto-hydrolysis isothermal time to 50 min and temperature to 180°C. According to the model, the theoretical values increase up to a maximum of 5.58 g/g for the same log R_0.

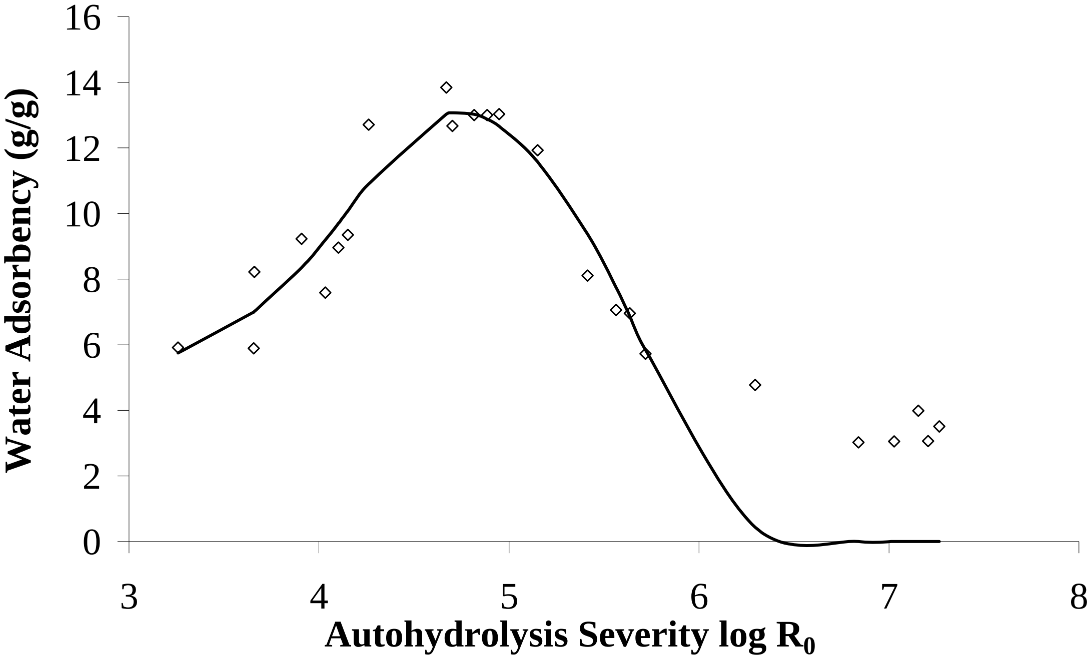


Fig. 9.12 Water adsorbency vs. the severity factor (for temperatures 160-240°C)

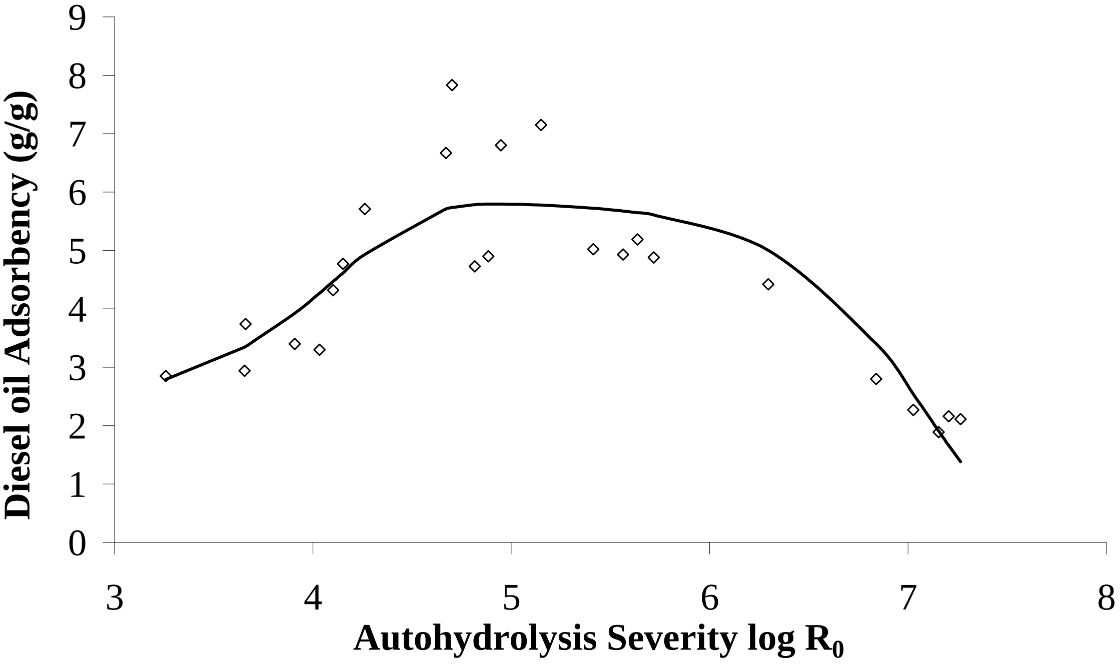


Fig. 9.13 Diesel oil adsorbency vs. the severity factor (for temperatures 160-240°C)

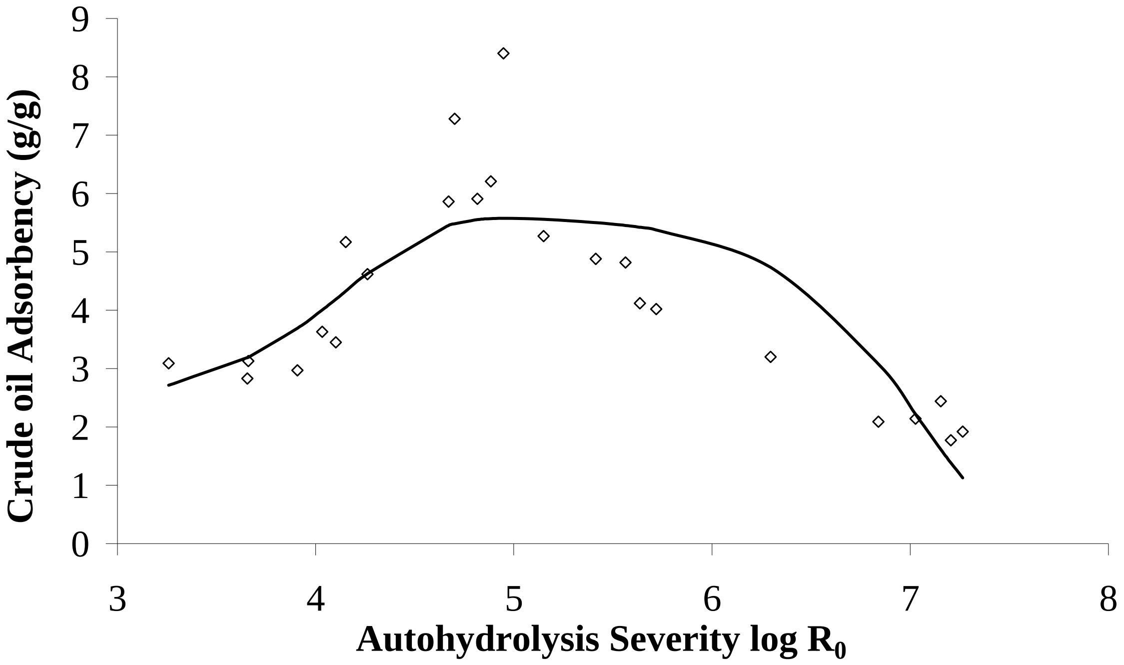


Fig. 9.14 Crude oil adsorbency vs. the severity factor (for temperatures 160-240°C)

Oil spill on freshwater

Auto-hydrolyzed wheat straw's adsorbency in the case of oil (diesel and crude oil) spills on freshwater and seawater was examined by Sidiras, D., Batzias, F., Konstantinou, I., Tsapatsis, M., (2014), in the study "Simulation of auto-hydrolysis effect on adsorptivity of wheat straw in the case of oil spill cleaning" which was published by the Chemical Engineering Research and Design Journal. Water, diesel, crude oil, total, RDA and RCA adsorbency of untreated and modified wheat straw in the cases of oil spills on freshwater/seawater are given in Table 9.1.

The experimental results of the water, oil (diesel oil/ crude oil), total, RDA and RCA adsorbency of the untreated (UWS) and the auto-hydrolyzed wheat straw (AWS) in the case of oil spills on freshwater are shown in the following diagrams.

In Fig. 9.15, the water, A_{WDF}, diesel, A_{DDF}, and total, A_{TDF}, adsorbencies, in the case of diesel oil spill in freshwater, are presented as functions of log R_0. The theoretical adsorbency values curve is estimated by eq. (8.2) for $i=W$, $j=D$ and $k=F$ in the case of water and for $i=D$, $j=D$ and $k=F$ in the case of diesel. The experimental and the theoretical total adsorbency values, A_{TDF}, were estimated according to the following simple equation:

$$A_{Tjk} = A_{Djk} + A_{Wjk} \tag{9.4}$$

where: j=D and k=F for Fig. 9.15. The experimental A_{DDF} values are shown to increase up to a maximum of 7.30 g/g for log R_0=4.88. According to the model, the theoretical A_{DDF} values increase up to a maximum of 6.14 g/g for log R_0=5.15. The experimental and theoretical A_{WDF} and A_{TDF} values do not show a maximum at the same log R_0.

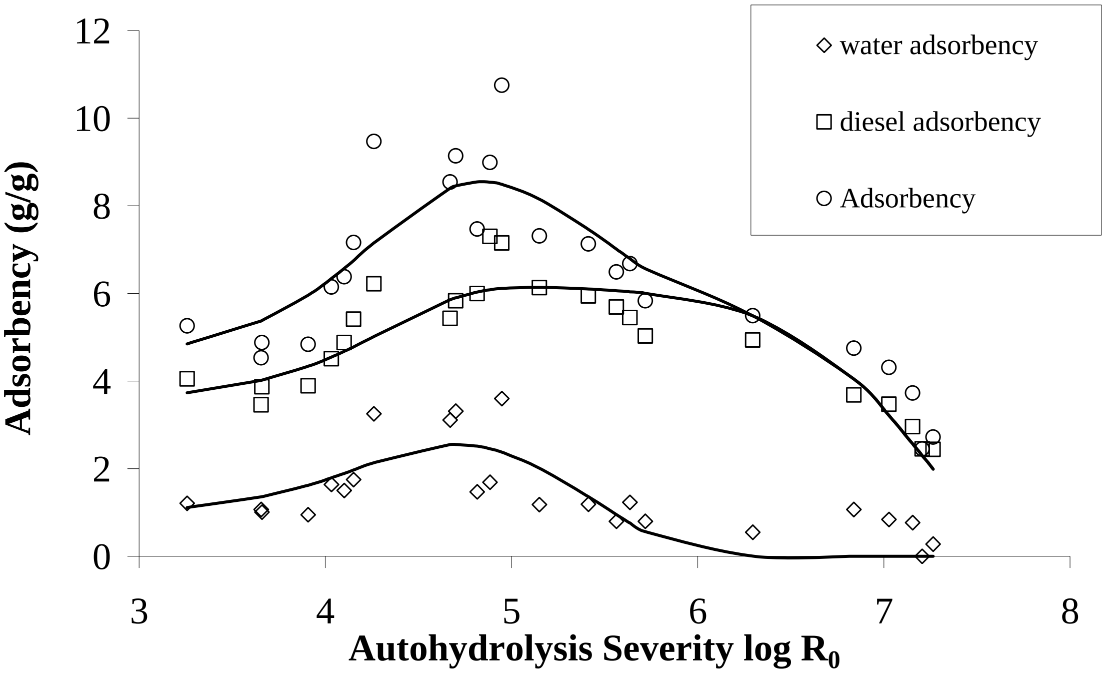


Fig. 9.15 Water, diesel and total adsorbency vs. the severity factor (reaction ending temperatures 160-240°C, diesel oil spill in freshwater)

The relative diesel adsorbency RDA is presented in Fig. 9.16 and gives no maximum at these conditions, e.g. is 83.9% for log R_0=5.15. The experimental and the theoretical RDA values were estimated according to the following simple equation:

$$RDA_{jk} = \left(A_{Djk} / A_{Tjk}\right) \cdot 100 \tag{9.5}$$

where: j=D and k=F for Fig. 9.16.

In Fig. 9.17, the water, A_{WCF}, crude oil, A_{CCF}, and total, A_{TCF}, adsorbencies, in the case of crude oil spill in freshwater, are presented as functions of log R_0. The theoretical adsorbency values curve is estimated by eq. (8.2) for *i=W, j=C* and *k=F* in the case of water and for *i=C, j=C* and *k=F* in the case of crude oil.

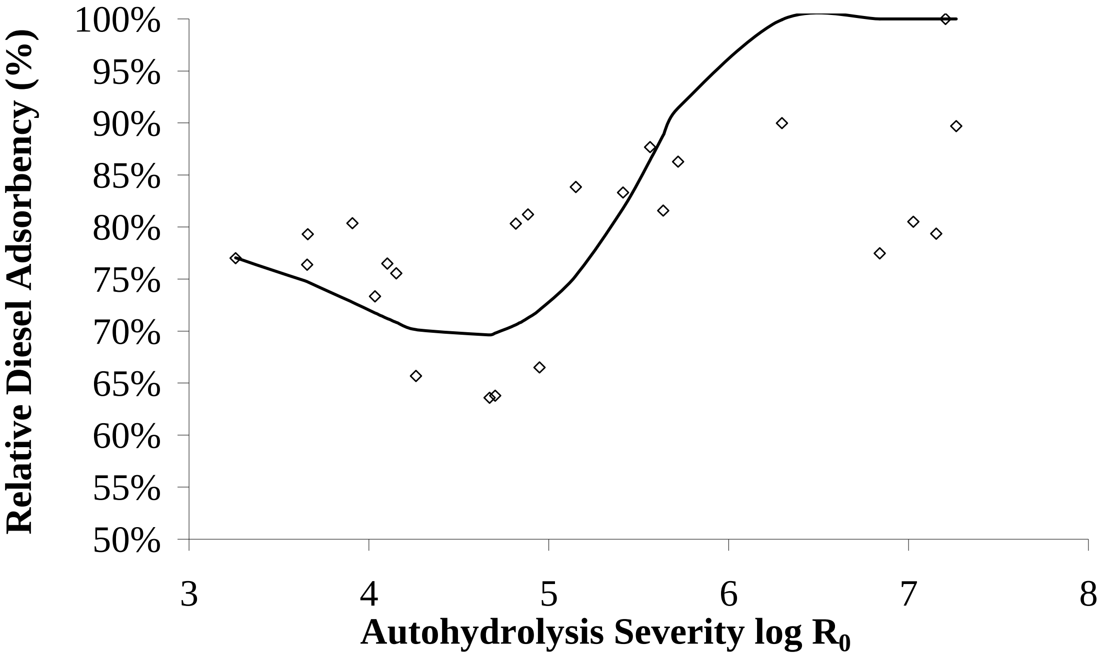


Fig. 9.16 RDA vs. the severity factor (for temperatures 160-240^oC, DOS in freshwater)

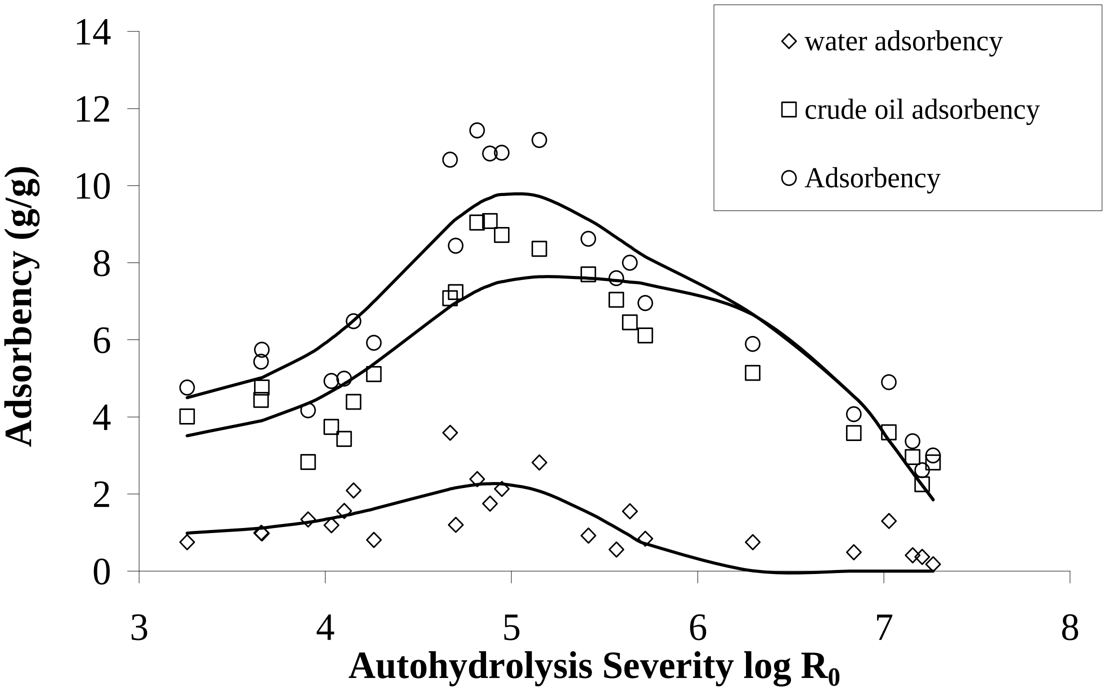


Fig. 9.17 Water, crude oil and total adsorbency vs. the severity factor (reaction ending temperatures 160-240^oC, crude oil spill in freshwater)

The experimental and the theoretical total adsorbency values, A_{TCF}, were estimated according to eq. (9.4) for $j=C$ and $k=F$. The experimental A_{CCF} values are shown to increase up to a maximum of 9.08 g/g for log R_0=4.88.

According to the model, the theoretical A_{CCF} values increase up to a maximum of 7.64 g/g for log R_0=5.15. The experimental and theoretical A_{WCF} and A_{TCF} values do not show a maximum at the same log R_0.

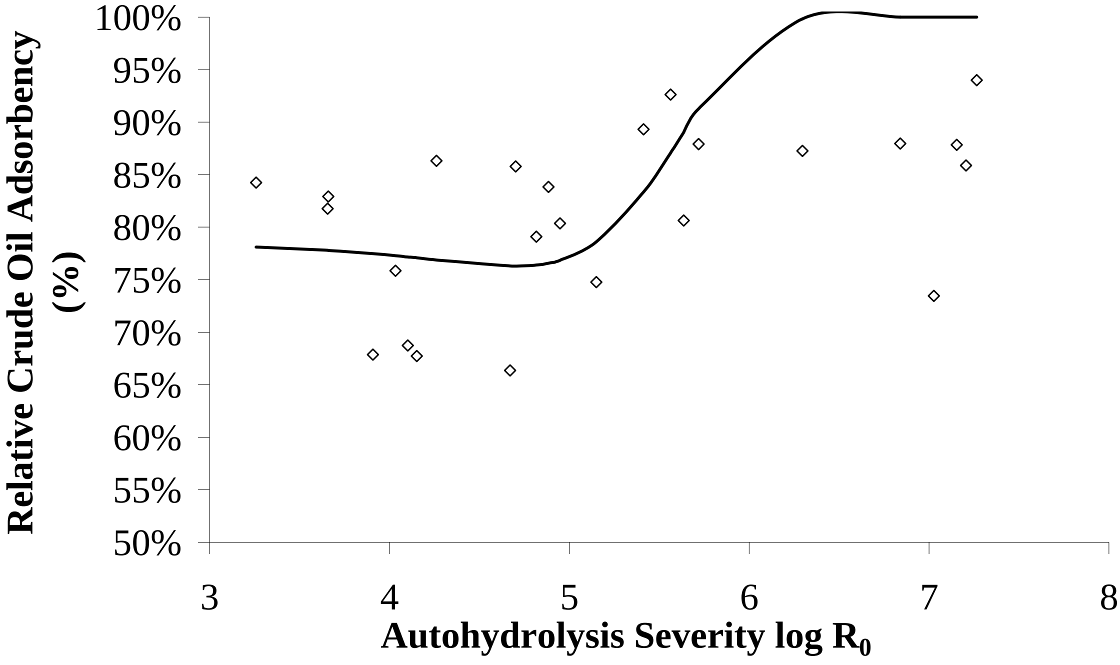


Fig. 9.18 RCA vs. the severity factor (for temperatures 160-240°C, COS in freshwater)

The relative crude oil adsorbency RCA is presented in Fig. 9.18 and gives no maximum at these conditions, e.g. is 83.8% for log R_0=4.88. The experimental and the theoretical RCA values were estimated according to the following simple equation:

$$RCA_{jk} = \left(A_{Cjk} / A_{Tjk}\right)\cdot 100 \qquad (9.6)$$

where: $j=C$ and $k=F$ for Fig. 9.18.

Oil spill on seawater

The experimental results of the water, oil (diesel oil/ crude oil), total, RDA and RCA adsorbency of the untreated (UWS) and the auto-hydrolyzed wheat straw (AWS) in the case of oil spills on seawater are shown in the following diagrams.

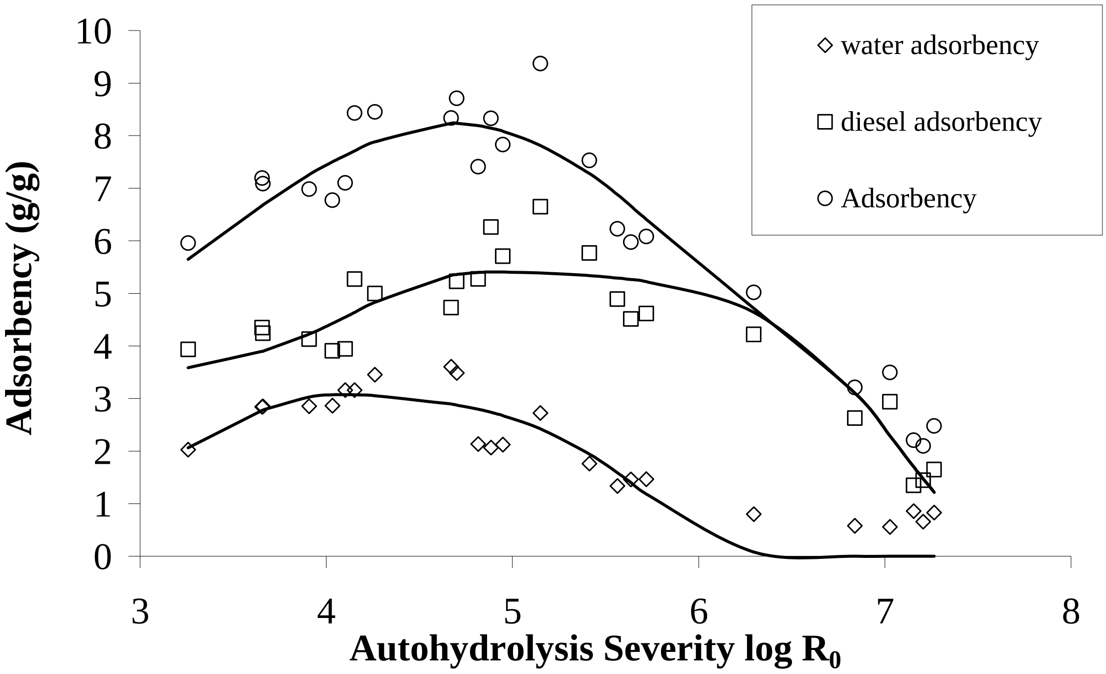


Fig. 9.19 Water, diesel and total adsorbency vs. the severity factor (reaction ending temperatures 160-240^{o}C, diesel oil spill in seawater)

In Fig. 9.19, the water, A_{WDS}, diesel, A_{DDS}, and total, A_{TDS}, adsorbencies, in the case of diesel oil spill in seawater, are presented as functions of log R_0. The theoretical adsorbency values curves are estimated by eq. (8.2) for $i=W$, $j=D$ and $k=S$ in the case of water and for $i=D$, $j=D$ and $k=S$ in the case of diesel. The experimental and the theoretical total adsorbency values, A_{TDS}, were estimated according to eq. (9.4) for $j=D$ and $k=S$.

The experimental A_{DDS} values are shown to increase up to a maximum of 6.65 g/g for log R_0=5.15. According to the model, the theoretical A_{DDS} values increase up to a maximum of 5.41 g/g for log R_0=4.95. The experimental and theoretical A_{WDS} and A_{TDS} values do not show a maximum at the same log R_0.

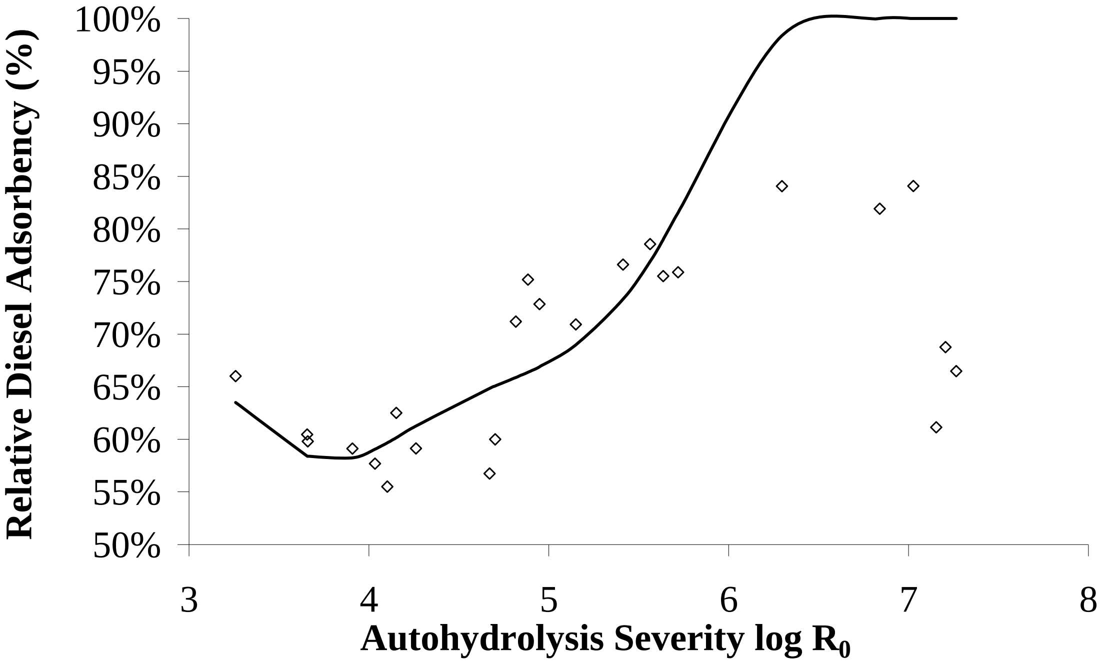


Fig. 9.20 RDA vs. the severity factor (for temperatures 160-240°C, DOS in seawater)

The relative diesel adsorbency RDA is presented in Fig. 9.20 and gives no maximum at these conditions, e.g. is 72.9% for log R_0=4.95. The experimental and the theoretical RDA values were estimated according to the eq. (9.6) where: $j=D$ and $k=S$.

In Fig. 9.21, the water, A_{WCS}, crude oil, A_{CCS}, and total, A_{TCS}, adsorbencies, in the case of crude oil spill in seawater, are presented as functions of log R_0. The theoretical adsorbency values curves are estimated by eq. (8.2) for $i=W$, $j=C$ and $k=S$ in the case of water and for $i=C$, $j=C$ and $k=S$ in the case of crude oil. The experimental and the theoretical total adsorbency values, A_{TCS}, were estimated according to eq. (9.4) for $j=C$ and $k=S$.

The experimental A_{CCS} values are shown to increase up to a maximum of 6.91 g/g for log R_0=5.15. According to the model, the theoretical A_{CCS} values increase up to a maximum of 5.30 g/g for log R_0=5.15. The experimental and theoretical A_{WCS} and A_{TCS} values do not show a maximum at the same log R_0.

The relative crude oil adsorbency RCA is presented in Fig. 9.22 and gives no maximum at these conditions, e.g. is 79.7% for log R_0=5.15.

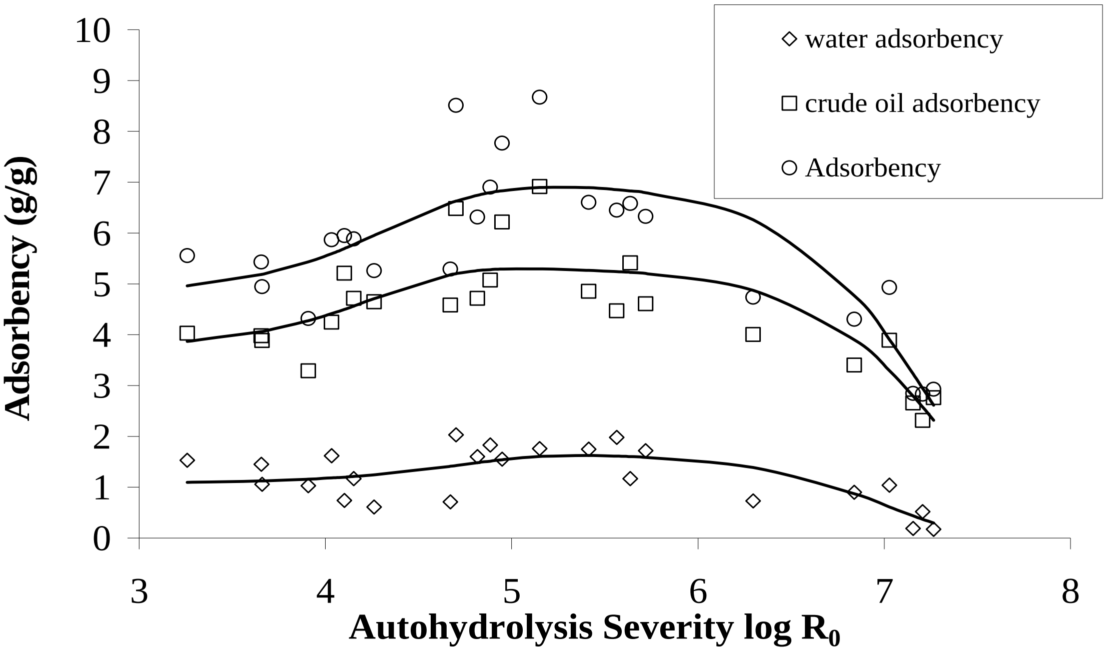


Fig. 9.21 Water, crude oil and total adsorbency vs. the severity factor (reaction ending temperatures 160-240^{o}C, crude oil spill in seawater)

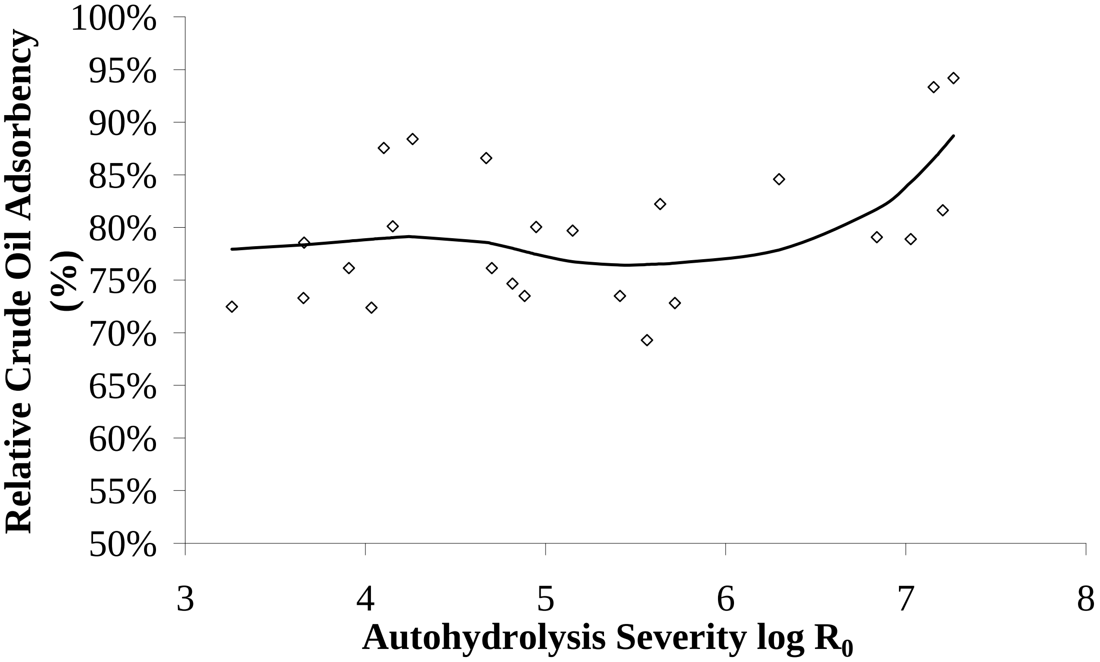


Fig. 9.22 RCA vs. the severity factor (for temperatures 160-240^{o}C, COS in seawater)

The experimental and the theoretical RDA values were estimated according to the eq. (9.6) where: j=C and k=S. In all the above cases, the empirical constants' values a_{1ijk}, b_{1ijk}, a_{2ijk}, b_{2ijk} were estimated using non linear regression analysis (NLRA). These values and the standard errors of estimate (SEE) values are presented in Table 9.2.

Table 9.2 The values of $A'_{\infty,ijk}$, b_{1ijk}, $A_{0,ijk}$ and b_{2ijk} of eq. (9.3) estimated using NLRA, and SEE-values

ijk	$A'_{\infty,ijk}$	b_{1ijk}	$A_{0,ijk}$	b_{2ijk}	SEE
WPN	470.8	$1.79 \cdot 10^{-6}$	4.79	$5.77 \cdot 10^{-5}$	2.0521
DPN	5528.1	$7.83 \cdot 10^{-8}$	2.35	$7.42 \cdot 10^{-5}$	0.8678
CPN	4213.2	$8.75 \cdot 10^{-8}$	2.35	$6.55 \cdot 10^{-5}$	1.0586
WDF	47.3	$3.34 \cdot 10^{-6}$	0.93	$5.13 \cdot 10^{-5}$	0.7102
DDF	4508.3	$6.18 \cdot 10^{-8}$	3.53	$4.49 \cdot 10^{-5}$	0.6060
WCF	27.3	$2.87 \cdot 10^{-6}$	0.89	$2.66 \cdot 10^{-5}$	0.6587
CCF	3533.9	$7.77 \cdot 10^{-8}$	3.23	$3.55 \cdot 10^{-5}$	1.0628
WDS	684.4	$1.88 \cdot 10^{-6}$	0.88	$4.08 \cdot 10^{-4}$	0.5173
DDS	4508.1	$8.16 \cdot 10^{-8}$	3.34	$6.75 \cdot 10^{-5}$	0.5809
WCS	327.5	$9.42 \cdot 10^{-8}$	1.08	$1.85 \cdot 10^{-5}$	0.3904
CCS	6180.3	$4.53 \cdot 10^{-8}$	3.72	$5.25 \cdot 10^{-5}$	0.7015

9.4 Acid hydrolyzed wheat straw adsorbencies

Pure liquids

Acid-hydrolyzed wheat straw's adsorbency was examined by D.K. Sidiras, and I.G. Konstantinou, (2012), in the study "A new oil spill adsorbent from sulphuric acid modified wheat straw", which was presented in the 5th WSEAS International Conference on Environmental and Geological Science and Engineering (EG '12) 2012, held in Vienna.

The experimental results of the water, diesel oil and crude oil adsorbency of the untreated (UWS) and the acid hydrolyzed wheat straw (AcWS) are presented in the following Figures.

The water adsorbency values for reaction ending temperature at 160°C were found to increase from 4.89 g/g to a maximum of 9.08 g/g for isothermal reaction time 0 min (Fig. 9.23).

The diesel oil adsorbency values for reaction ending temperature at 160°C were found to increase from 2.77 g/g to a maximum of 5.24 g/g for isothermal reaction time 20 min (Fig. 9.24).

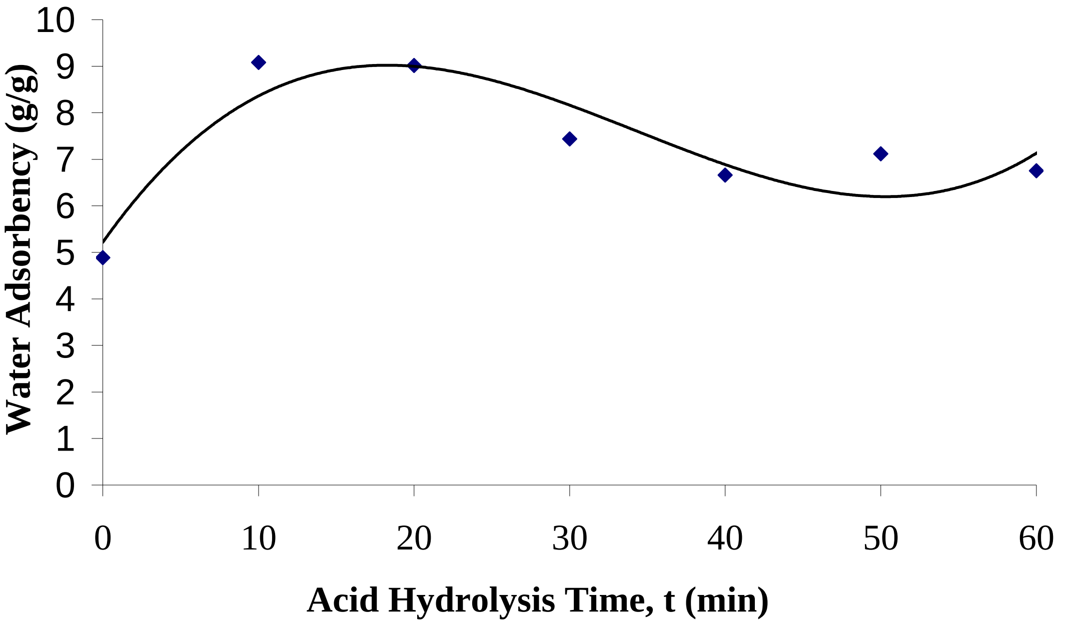


Fig. 9.23 AcWS water adsorbency values vs. the acid hydrolysis time for 160°C

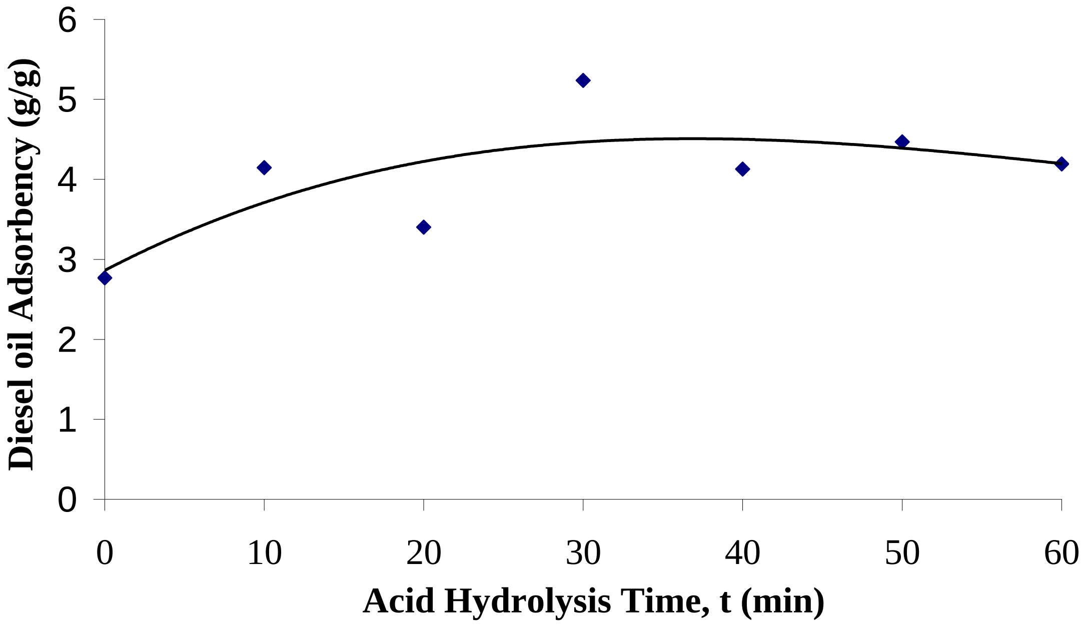


Fig. 9.24 AcWS diesel oil adsorbency values vs. the acid hydrolysis time for 160°C

The crude oil adsorbency values for reaction ending temperature at 160°C were found to increase from 2.82 g/g to a maximum of 5.38 g/g for isothermal reaction time the same with that in the case of diesel (Fig. 9.25).

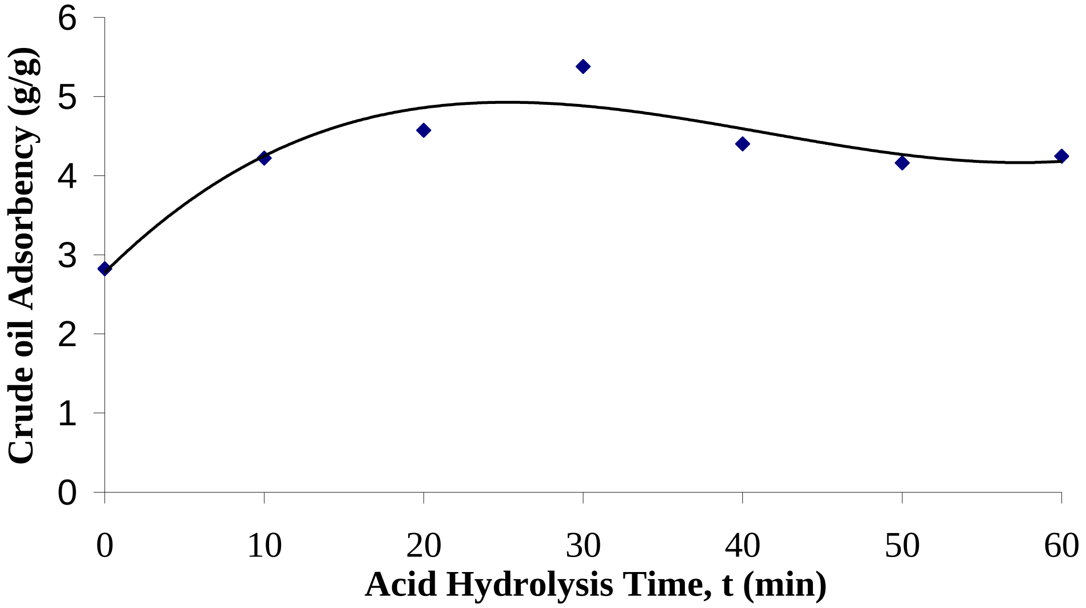


Fig. 9.25 AcWS crude oil adsorbency values vs. the acid hydrolysis time for 160^{o}C

At 180°C the maximum water adsorbency value was 7.05 g/g for isothermal reaction time 0 min (Fig. 9.26). At the same temperature the maximum diesel oil adsorbency value was 5.14 g/g for isothermal reaction time 30 min (Fig. 9.27). Moreover, the maximum crude oil adsorbency-value was 5.17 g/g for isothermal reaction time 0 min (Fig. 9.28).

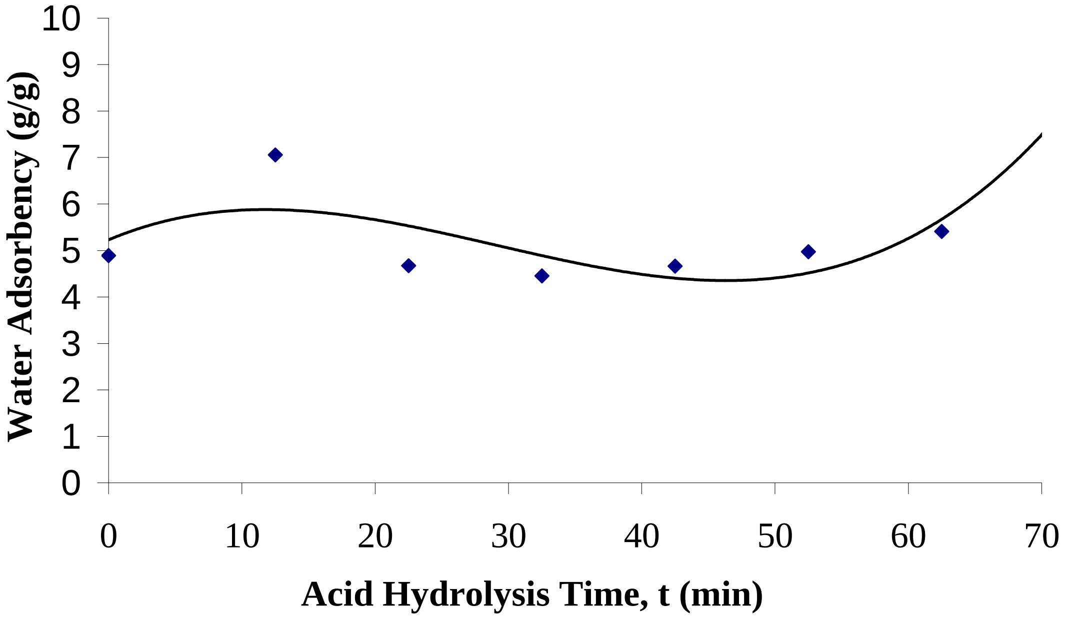


Fig. 9.26 AcWS water adsorbency values vs. the acid hydrolysis time for 180^{o}C

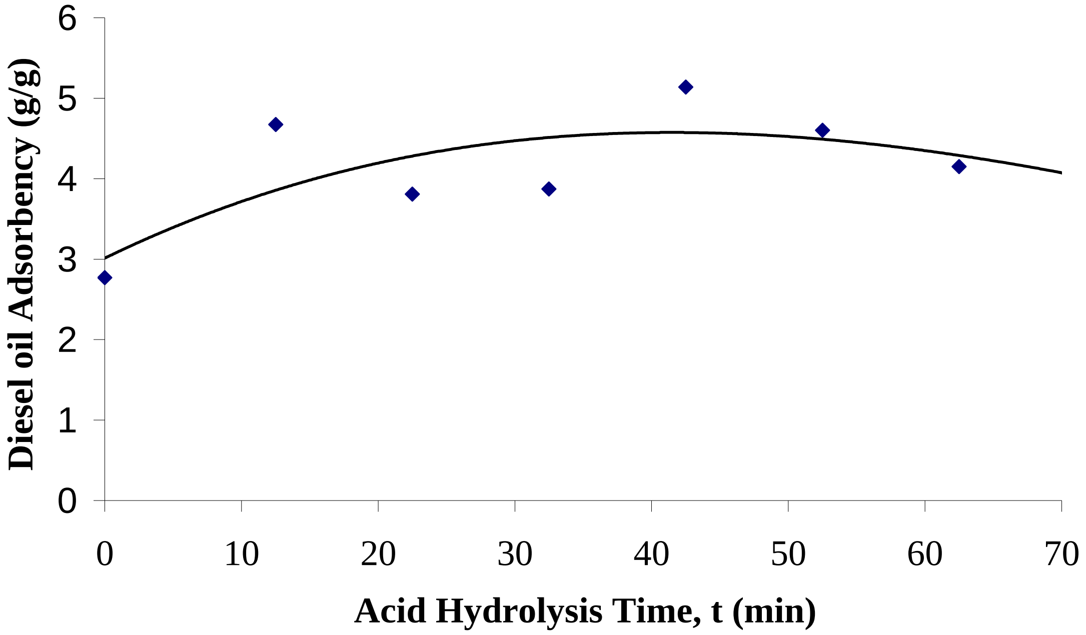


Fig. 9.27 AcWS diesel oil adsorbency values vs. the acid hydrolysis time for 180^{o}C

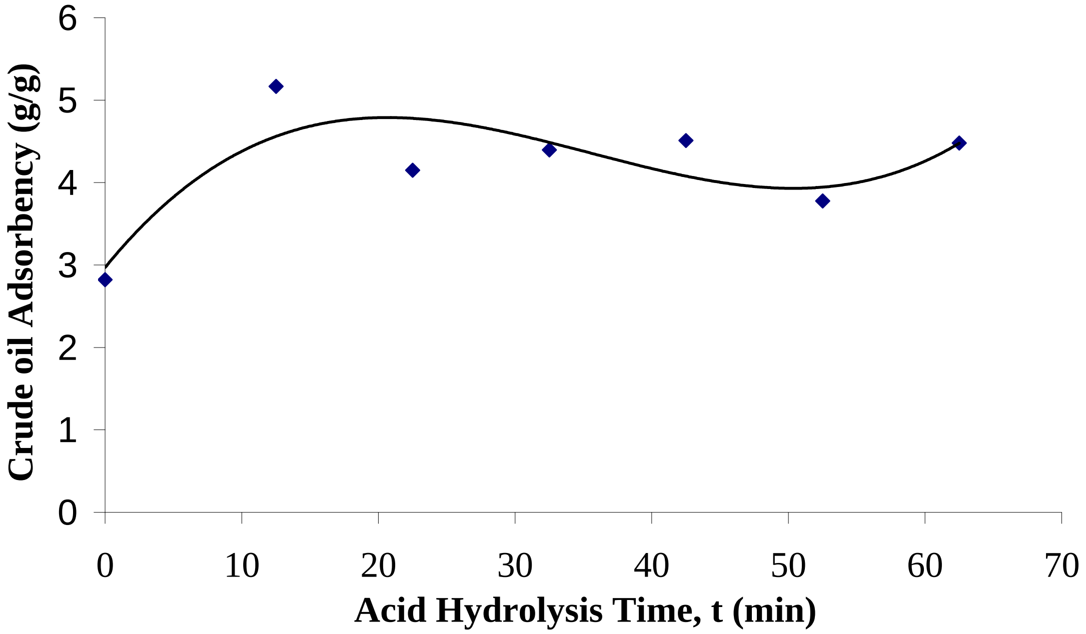


Fig. 9.28 AcWS crude oil adsorbency values vs. the acid hydrolysis time for 180^{o}C

At 200 and 220°C the water adsorbency was decreasing as low as 0.93 g/g for 50 min isothermal hydrolysis time (Figs. 9.29 and 9.30). At 200°C the maximum diesel oil adsorbency value was 4.16 g/g for isothermal reaction time 30 min (Fig. 9.31).

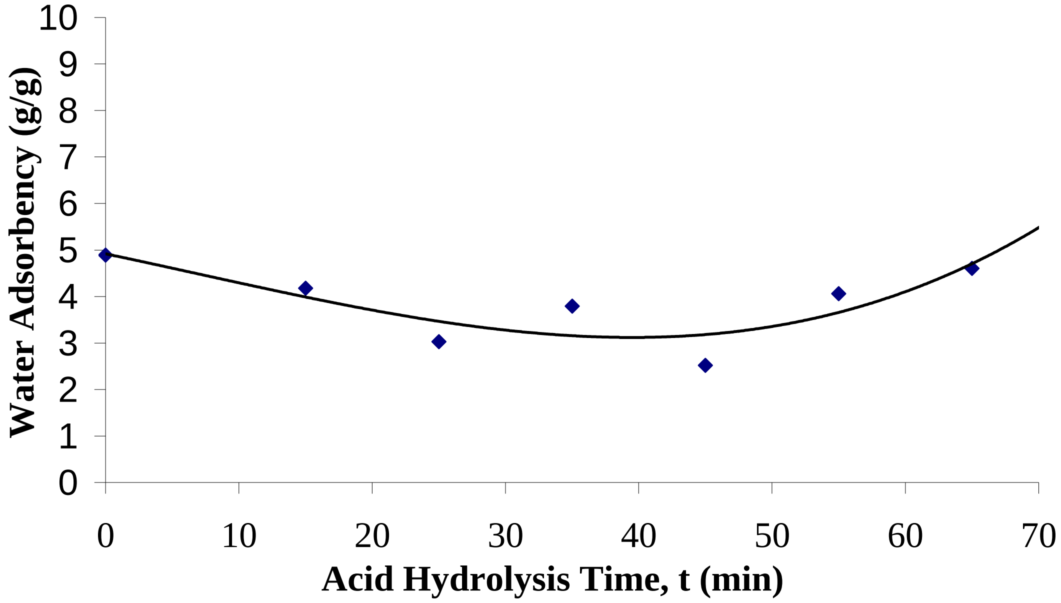


Fig. 9.29 AcWS water adsorbency values vs. the acid hydrolysis time for 200°C

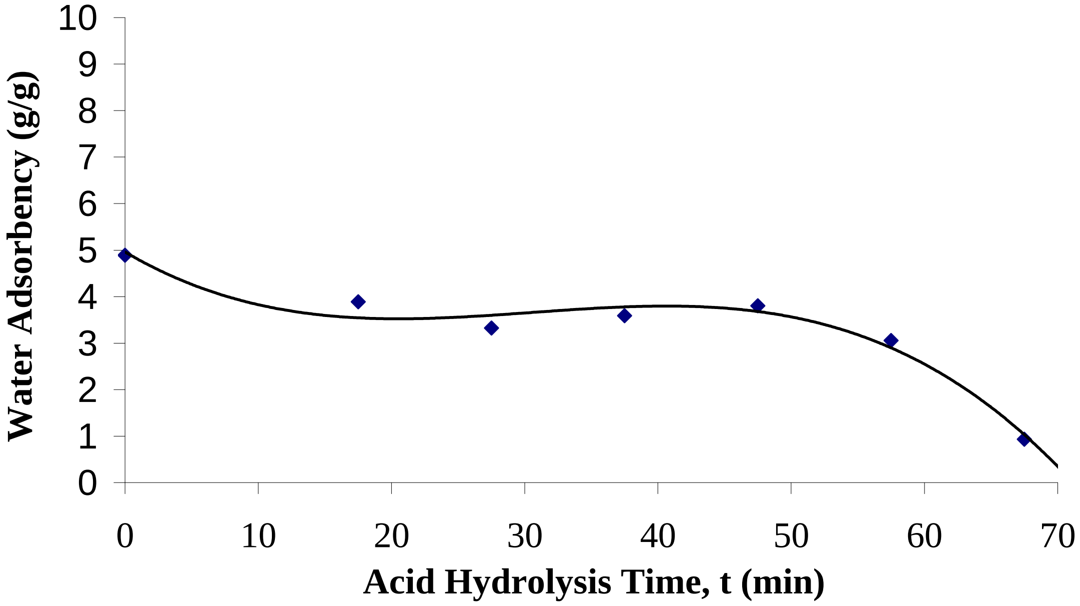


Fig. 9.30 AcWS water adsorbency values vs. the acid hydrolysis time for 220°C

At the same temperature the maximum crude oil adsorbency value was 5.16 g/g for isothermal reaction time 50 min (Fig. 9.32). At 220°C the maximum diesel oil adsorbency value was 4.76 g/g for isothermal reaction time 50 min (Fig. 9.33). At the same temperature the maximum crude oil adsorbency value was 4.78 g/g for isothermal reaction time 50 min (Fig. 9.34).

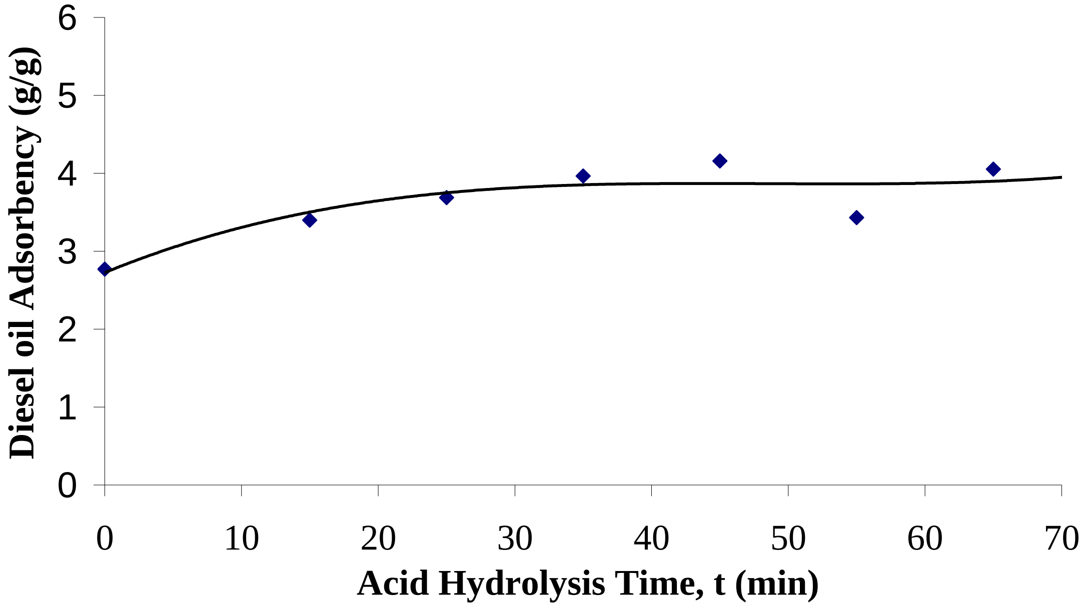


Fig. 9.31 AcWS diesel oil adsorbency values vs. the acid hydrolysis time for 200°C

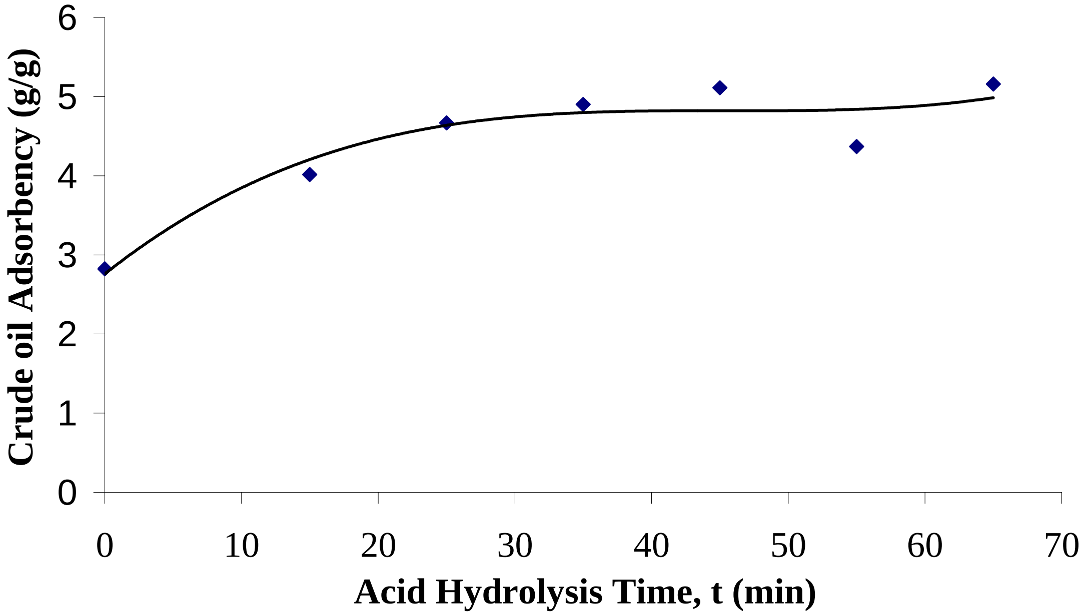


Fig. 9.32 AcWS crude oil adsorbency values vs. the acid hydrolysis time for 200°C

The water, diesel oil and crude oil adsorbency can be given as function of the autohydrolysis time as follows:

$$A_i = a_i t^3 + b_i t^2 + c_i t + d_i \tag{9.7}$$

where: *A* is the adsorbency (g/g), *t* is the acid hydrolysis time (min), and *i*=*W*, *D*, *C*; *W* is for Water, *D* is for Diesel oil and *C* is for Crude oil.

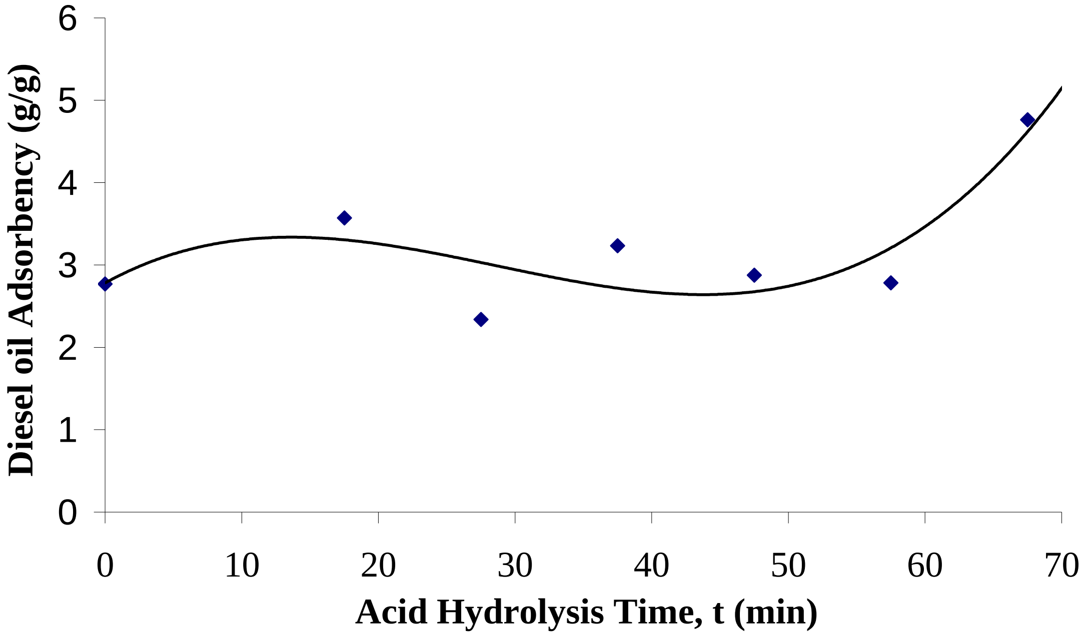


Fig. 9.33 AcWS diesel oil adsorbency values vs. the acid hydrolysis time for 220^{o}C

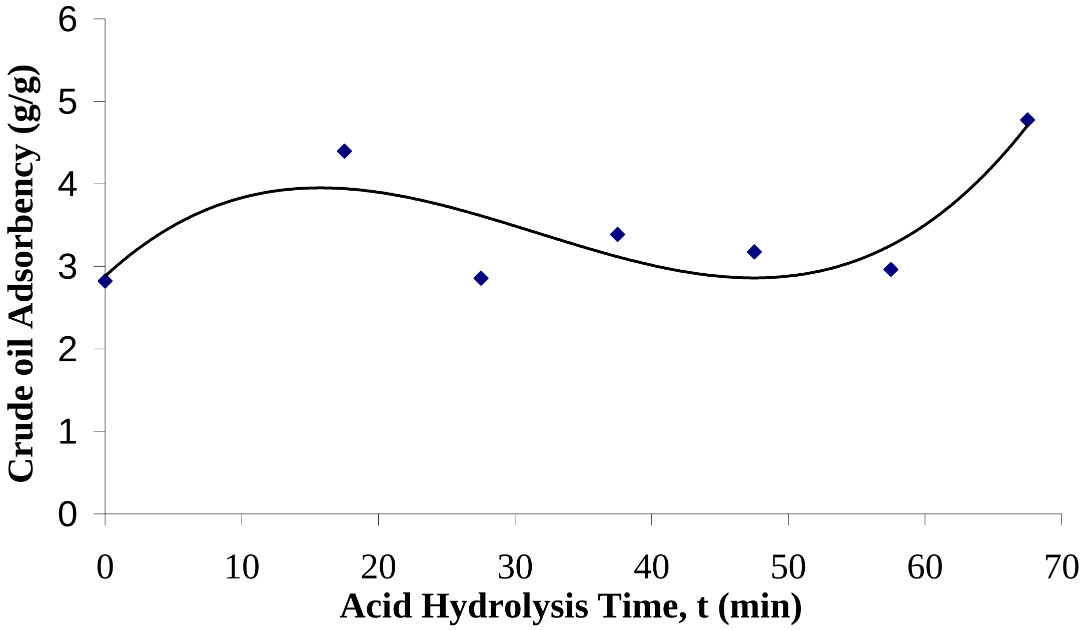


Fig. 9.34 AcWS crude oil adsorbency values vs. the acid hydrolysis time for 220^{o}C

The values of the coefficients of eq. (9.7) are given in Table 9.3. At the same Table the correlation coefficients are presented.

Table 9.3 Coefficients of eq. (9.7) and correlation coefficients R^2

T (°C)	I	a_i	b_i	c_i	d_i	R^2
160	W	0	-0.017	0.473	5.217	0.826
180	W	7.10^{-5}	-0.006	0.121	5.228	0.416
200	W	2.10^{-5}	0.000	-0.060	4.917	0.708
220	W	-7.10^{-5}	0.006	-0.168	4.959	0.968
160	D	1.10^{-5}	-0.002	0.103	2.862	0.562
180	D	4.10^{-6}	-0.001	0.082	3.012	0.518
200	D	1.10^{-5}	-0.001	0.071	2.725	0.769
220	D	5.10^{-5}	-0.004	0.090	2.782	0.721
160	C	5.10^{-5}	-0.005	0.199	2.775	0.888
180	C	7.10^{-5}	-0.007	0.204	2.970	0.687
200	C	2.10^{-5}	-0.003	0.136	2.759	0.904
220	C	7.10^{-5}	-0.006	0.153	2.880	0.718

The water adsorbency values for AcWS decrease as $\log R_0$ increases (Fig. 9.35). On the other hand, the experimental data shows an increase from 4.9 g/g to 9.1 g/g for mild acid treatment at 160°C for 0 min.

AcWS shows maximum diesel oil adsorbency value equal to 4.4 g/g at Severity Factor $\log R_0 = 4.3$ (Fig. 9.36). According to the simulation model maximum diesel oil adsorbency value was 4.4 g/g for $\log R_0 = 4.3$ (i.e., 180°C for 10 min), while according to the experimental data maximum adsorbency was 5.2 g/g for $\log R_0 = 3.9$ (i.e., 160°C for 20 min).

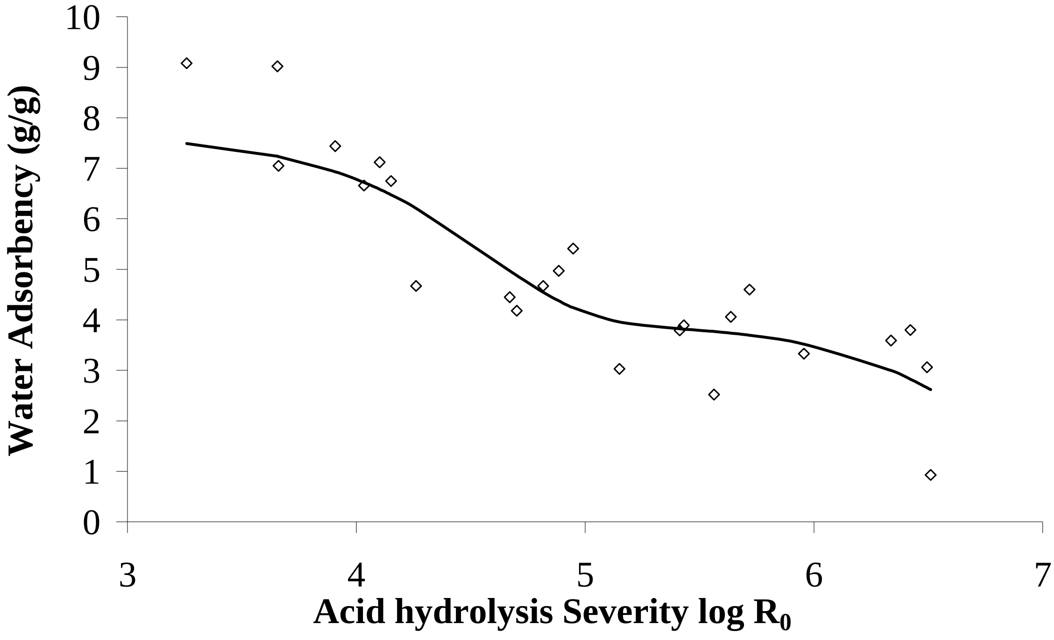


Fig. 9.35 UWS and AcWS water adsorbency values vs. Severity Factor R_0

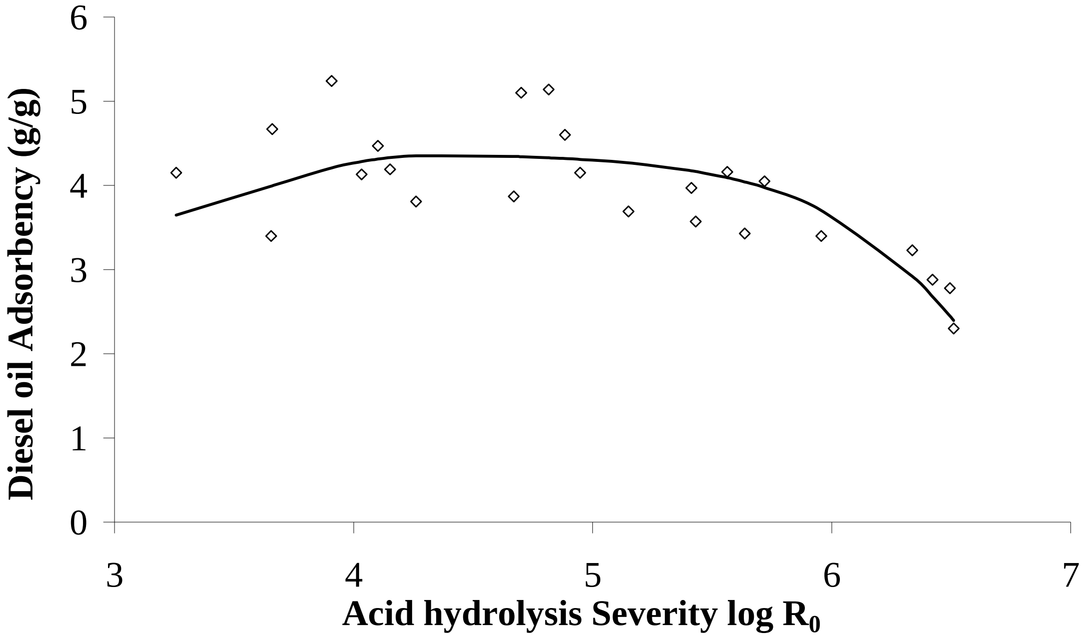


Fig. 9.36 UWS and AcWS diesel oil adsorbency values vs. Severity Factor R_0

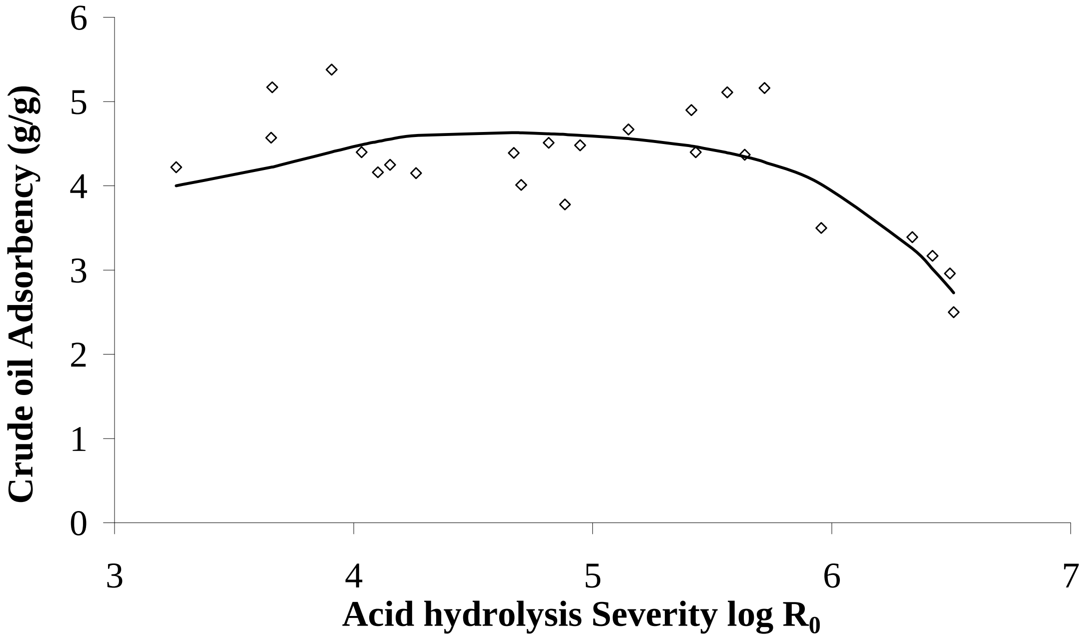


Fig. 9.37 UWS and AcWS crude oil adsorbency values vs. Severity Factor R_0

AcWS shows maximum crude oil adsorbency value equal to 4.6 g/g at Severity Factor $\log R_0 = 4.7$ (Fig. 9.37). According to the simulation model maximum crude oil adsorbency value was 4.6 g/g for $\log R_0 = 4.7$ (i.e., 180°C for 20 min), while according to the experimental data maximum adsorbency was 5.4 g/g for $\log R_0 = 3.9$ (i.e., 160°C for 20 min).

9.5 Autohydrolyzed barley straw adsorbencies

Pure liquids

Auto-hydrolyzed barley straw's adsorbency was examined by D.K. Sidiras, I.G. Konstantinou, T.K. Politi, (2011), in the study "Auto-hydrolysis modified barley straw as low cost adsorbent for oil spill cleaning", which was presented in the 19th European Biomass Conference and Exhibition 2011, held in Berlin. The experimental results of the water and oil adsorbency of the untreated (UBS) and the auto-hydrolyzed barley straw (ABS) are shown in the following diagrams. In Figure 9.38, the water adsorbency vs. the auto-hydrolysis time for reaction-ending temperatures of 160, 180, 200 and 240°C, showed an increasing trend as a function of the auto-hydrolysis time in the cases of 160 and 180°C, whereas the trend was decreasing at 240°C.

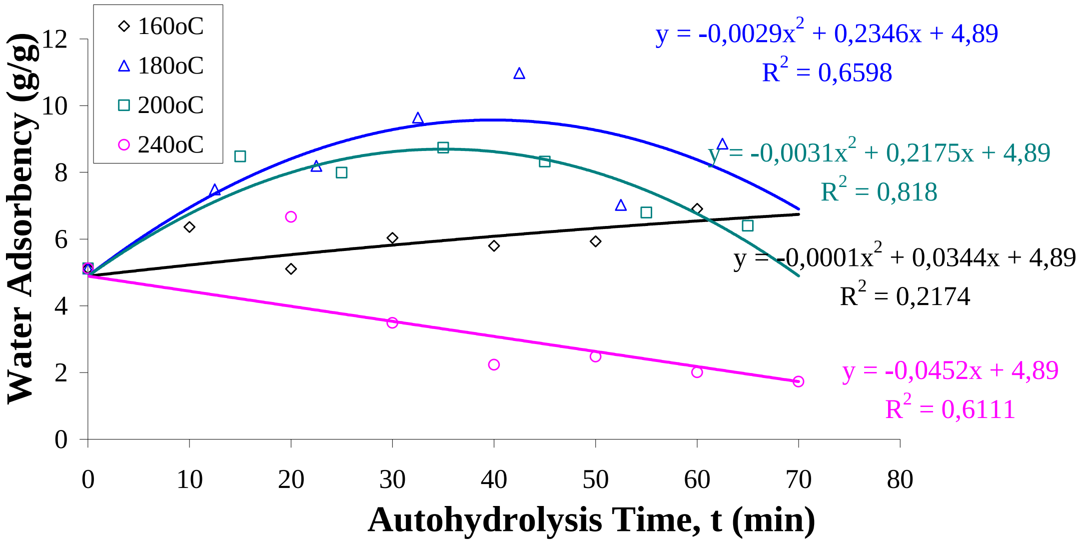


Fig. 9.38 UBS and ABS water adsorbency values vs. the auto-hydrolysis time

The water adsorbency at reaction-ending temperature of 200°C was increasing for auto-hydrolysis time less than 30 min and then decreased; the maximum of water adsorbency was about 11.0 g/g. The water adsorbency as a function of the (1-SRY), for reaction ending temperatures 160-240°C, is given in Figure 9.39. According to the Figure 9.40 data, diesel oil adsorbency as a function of the autohydrolysis time showed an increasing trend for reaction-ending temperatures 160 and 180°C, whereas the trend was decreasing at 240°C. The diesel oil adsorbency at reaction-ending temperature of 200°C was increasing for autohydrolysis time less than 35 min and then was decreasing; the maximum of diesel oil adsorbency was 6.9 g/g.

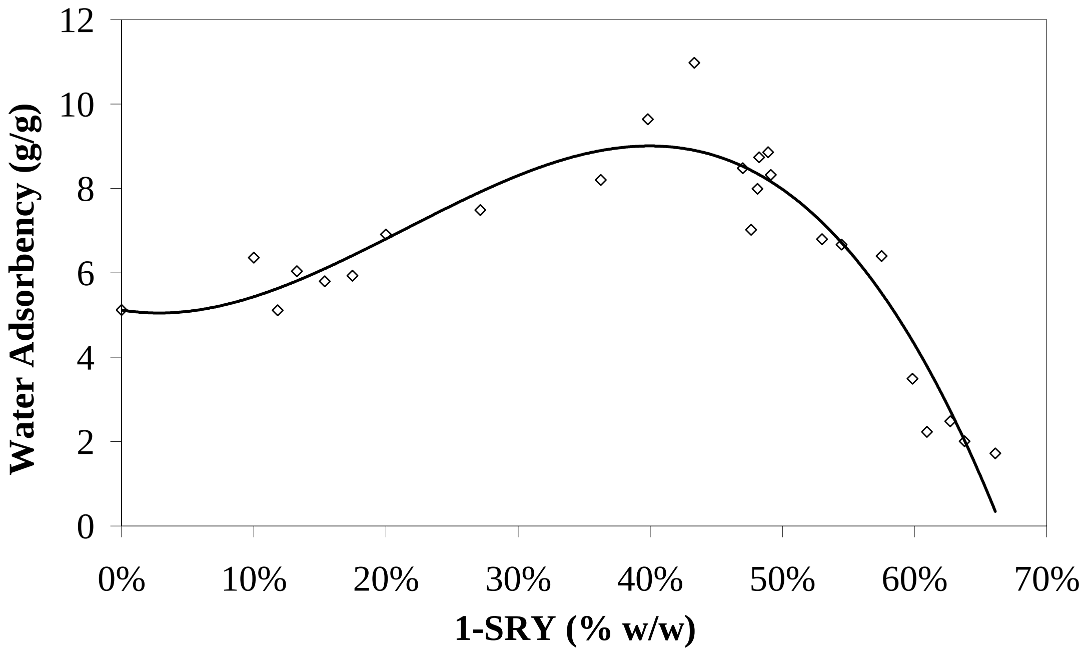


Fig. 9.39 Water adsorbency values vs. the (1-SRY) for temperatures 160-240°C

The diesel oil adsorbency as a function of the (1-SRY), for reaction ending temperatures 160-240°C, is given in Figure 9.41.

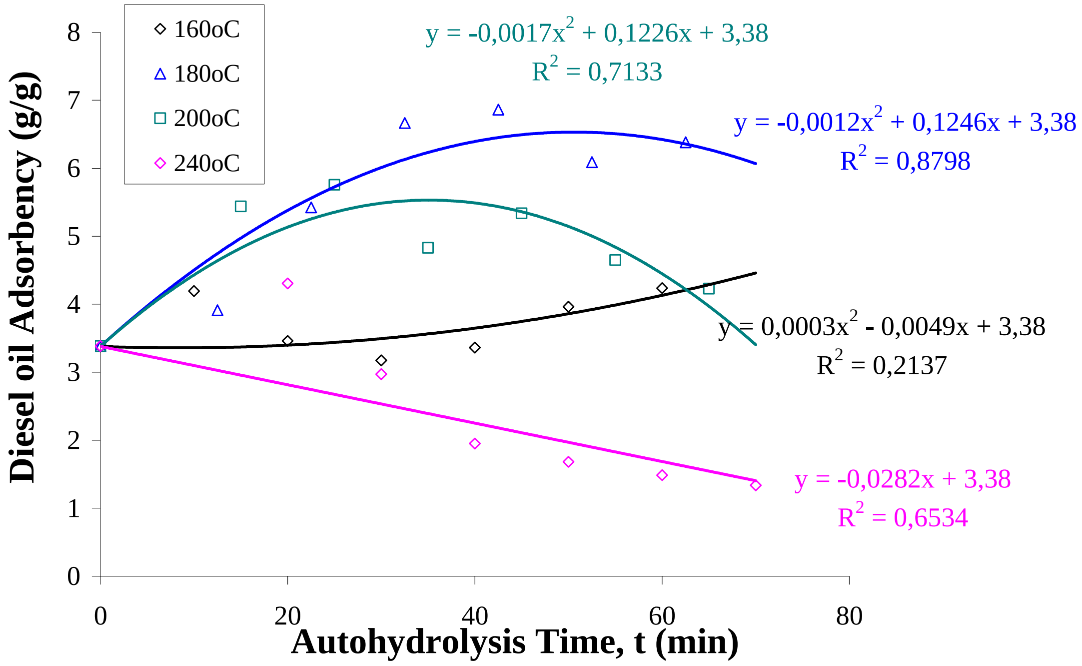


Fig. 9.40 UBS and ABS diesel oil adsorbency values vs. the auto-hydrolysis time

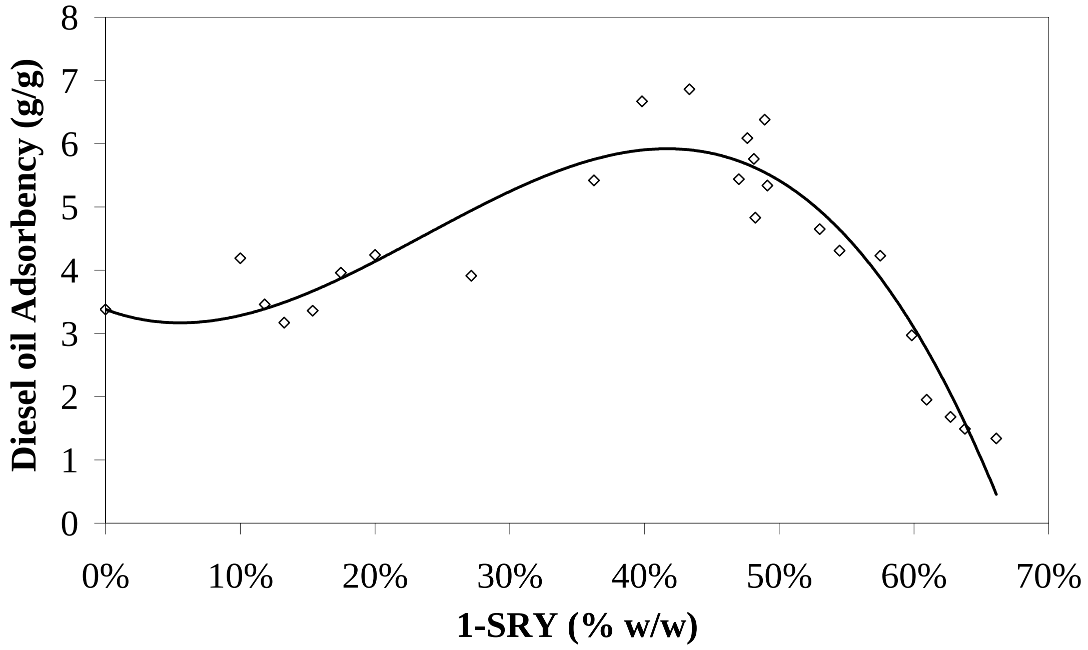


Fig. 9.41 Diesel oil adsorbency values vs. the (1-SRY) for temperatures 160-240°C

According to the Figure 9.42 data, crude oil adsorbency as a function of the auto-hydrolysis time was increasing for reaction-ending temperatures 160, and 180°C and decreasing for 240°C. Crude oil adsorbency was increasing for auto-hydrolysis time less than 35 min for reaction-ending temperatures 200°C, and then was decreasing. The maximum of crude oil adsorbency was 8.3 g/g.

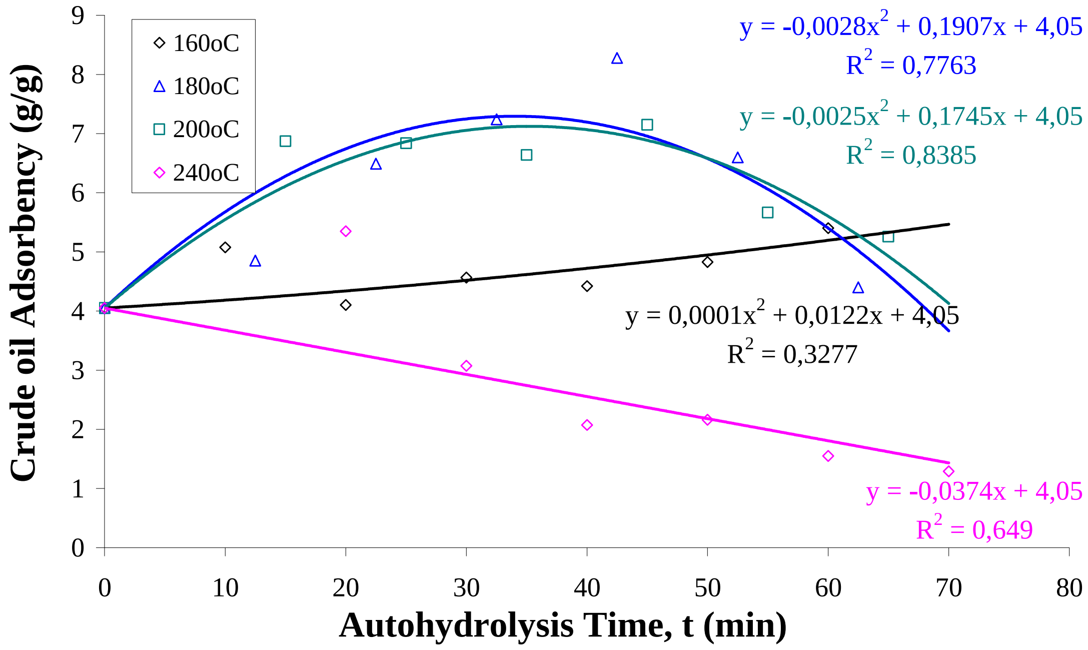


Fig. 9.42 UBS and ABS crude oil adsorbency values vs. the auto-hydrolysis time

The crude oil adsorbency as a function of the (1-SRY), for reaction ending temperatures 160-240^{o}C, is given in Figure 9.43. The water, diesel oil and crude oil adsorbency can be given as function of the auto-hydrolysis time as follows:

$$A_i = a_i t^2 + b_i t + c_i \qquad (9.8)$$

where: *A* is the adsorbency (g/g), *t* is the auto-hydrolysis time (min), and *i=W*, *D*, *C;* *W* is for Water, *D* is for Diesel oil and *C* is for Crude oil. The values of the coefficients of eq. (9.8) are given in Table 9.4.

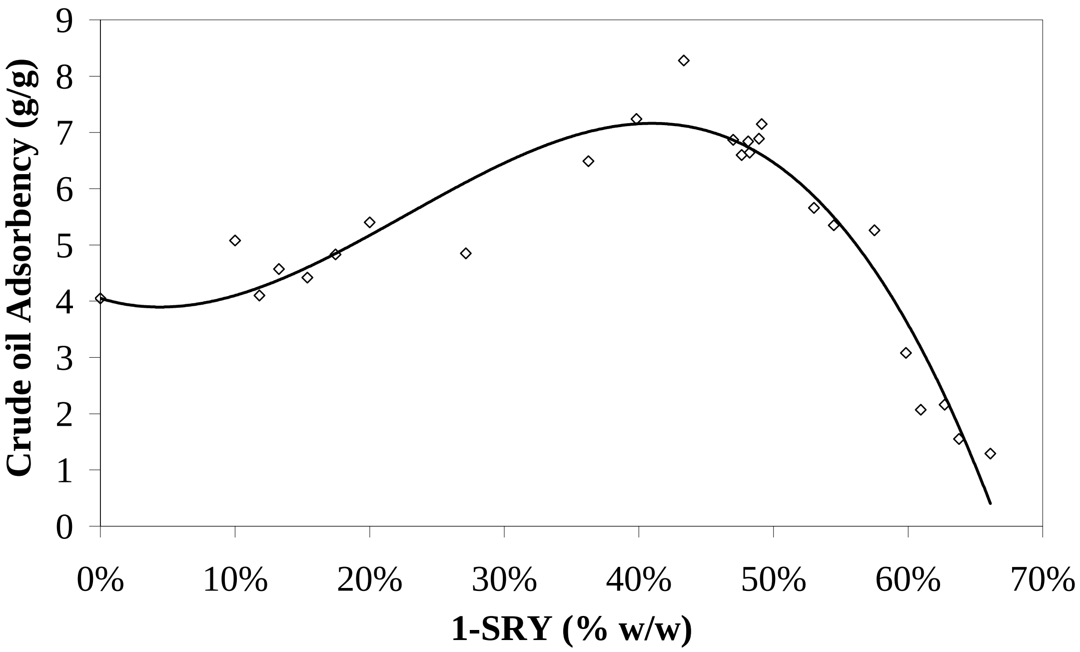


Fig. 9.43 Crude oil adsorbency values vs. the (1-SRY) for reaction ending temperatures 160-240^{o}C

Table 9.4 Coefficients of eq. (9.8)

T (^{o}C)	*i*	a_i	b_i	c_i	R^2
160	W	-0.0001	0.0344	4.89	0.2174
180	W	-0.0029	0.2346	4.89	0.6598
200	W	-0.0031	0.2175	4.89	0.8180
240	W	0.0000	-0.0452	4.89	0.6111
160	D	0.0003	-0.0049	3.38	0.2137
180	D	-0.0012	0.1246	3.38	0.8798
200	D	-0.0017	0.1226	3.38	0.7133
240	D	0.0000	-0.0282	3.38	0.6534
160	C	0.0001	0.0122	4.05	0.3277
180	C	-0.0028	0.1907	4.05	0.7763
200	C	-0.0025	0.1745	4.05	0.8385
240	C	0.0000	-0.0374	4.05	0.6490

The water, diesel oil and crude oil adsorbency can be given as function of the auto-hydrolysis solid residue yield – SRY or y (% w/w) as follows:

$$A_i = a_i^{'}(1-y)^3 + b_i^{'}(1-y)^2 + c_i^{'}(1-y) + d_i^{'} \tag{9.9}$$

The values of the coefficients of eq. (9.9) are given in Table 9.5.

Table 9.5 Coefficients of eq. (9.9)

i	$a_{i'}$	$b_{i'}$	$c_{i'}$	$d_{i'}$	R^2
W	-154.8	99.34	- 5.252	5.12	0.8916
D	-116.5	82.49	- 8.053	3.38	0.8799
C	-133.7	91.02	- 7.255	4.05	0.9116

.

The diesel oil adsorbency shows a good linear correlation vs. the water adsorbency for all auto-hydrolysis reaction-ending temperatures (see Figure 9.44).

This adsorbency increasing-rate was higher for 180 and 240^{o}C auto-hydrolysis reaction-ending temperatures, when compared with the rates for 160 and 200^{o}C.

The crude oil adsorbency shows a significant linear correlation vs. the water adsorbency for auto-hydrolysis reaction-ending temperatures 160-240^{o}C (see Figure 9.45). The adsorbency increasing-rate was higher for auto-hydrolysis reaction-ending temperatures 200 and 240^{o}C compared with the rates at 160 and 180^{o}C.

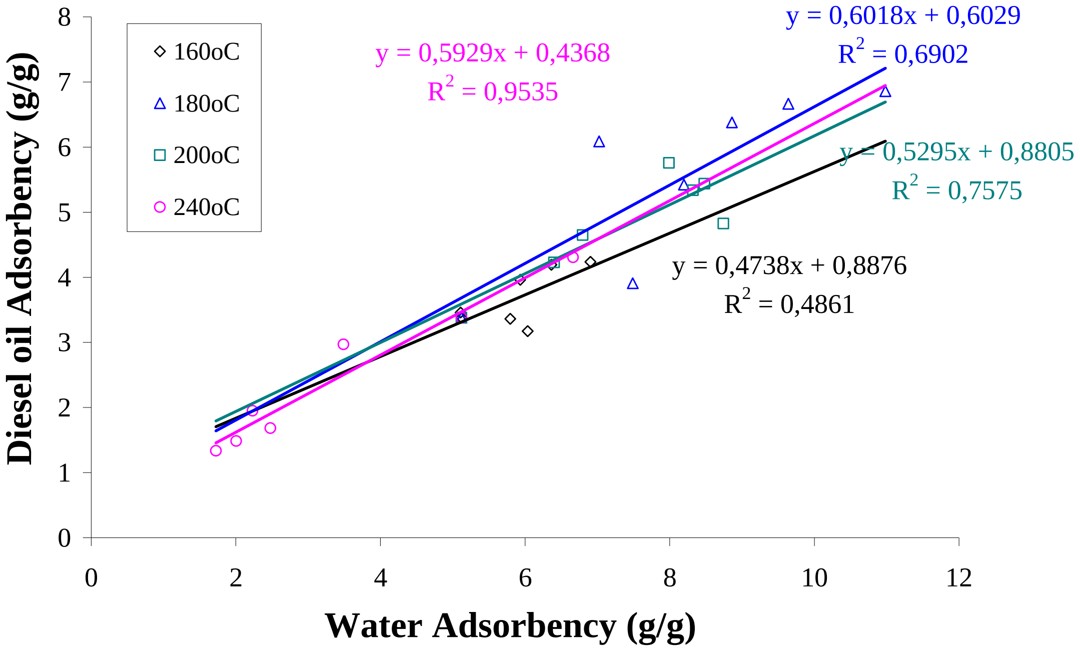


Fig. 9.44 Diesel oil adsorbency values vs. water adsorbency values

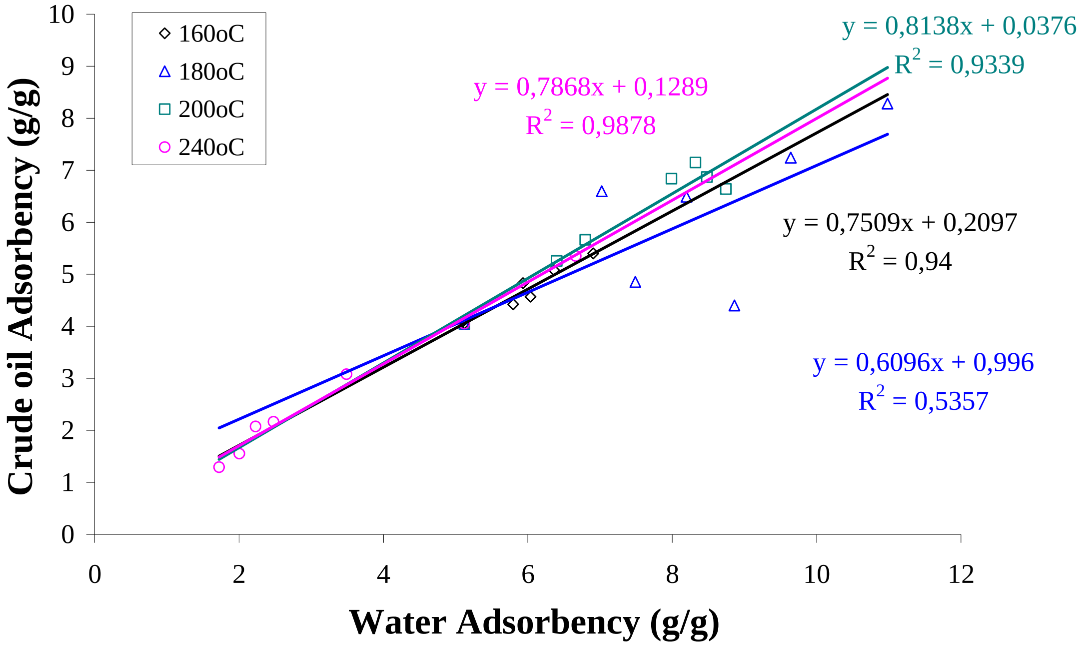


Fig. 9.45 Crude oil adsorbency values vs. water adsorbency values

Diesel oil adsorbency vs. water adsorbency (Figure 9.46), crude oil adsorbency vs. water adsorbency (Figure 9.47), and diesel oil adsorbency vs. crude oil adsorbency (Figure 9.48) are given for the auto-hydrolysis reaction-ending temperatures range from 160 to 240°C. The linear correlation coefficients were relatively high indicating linear correlation between these adsorbency values.

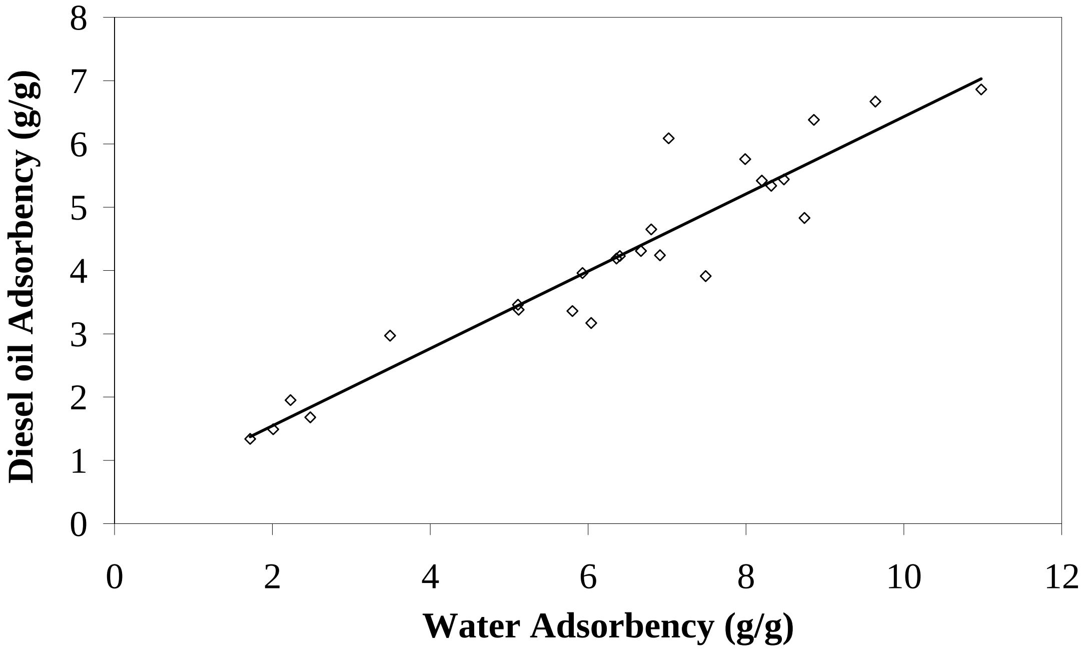


Fig. 9.46 Diesel oil adsorbency values vs. water adsorbency values

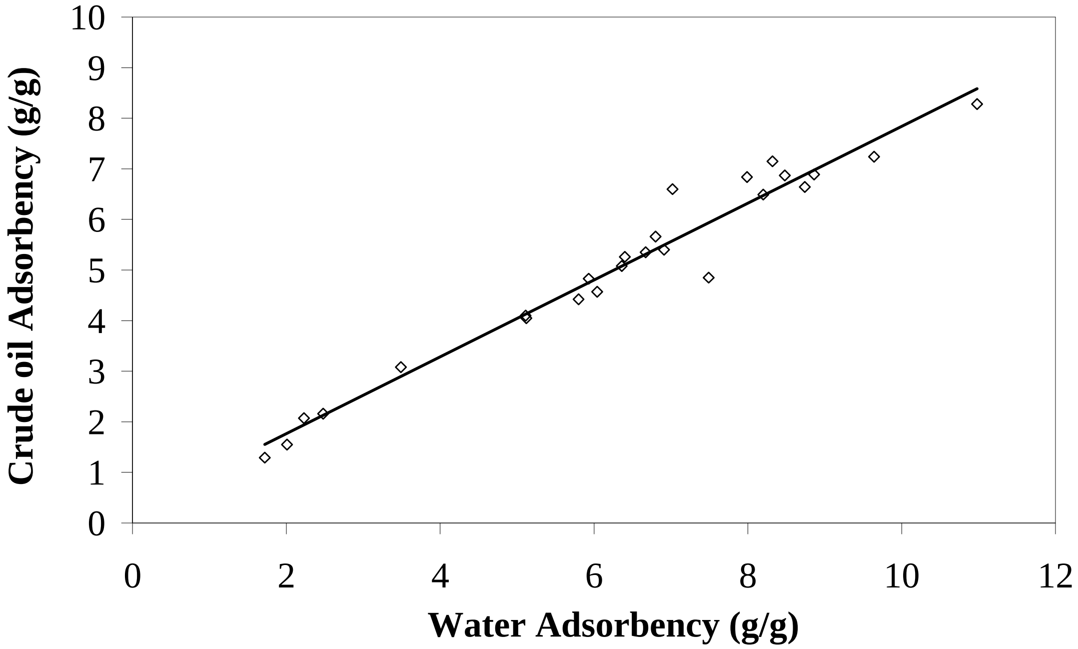


Fig. 9.47 Crude oil adsorbency values vs. water adsorbency values

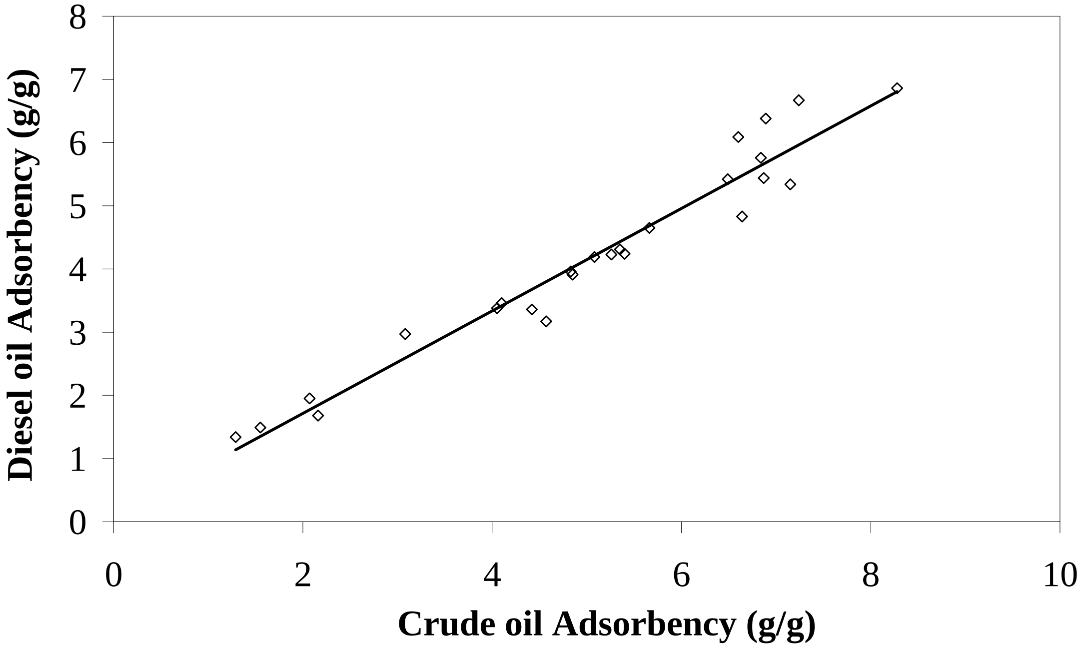


Fig. 9.48 Diesel oil adsorbency values vs. crude oil adsorbency values

The Water-Diesel oil (WD), Water-Crude oil (WC) and Crude oil-Diesel oil (CD) Adsorbency values correlation can be given as follows:

$$A_j = a_{ij} A_i + b_{ij} \tag{9.10}$$

The values of the coefficients of eq. (9.10) are given in Table 9.6. The ABS shows maximum water adsorbency value equal to 8.4 g/g at Severity Factor logR_0 = 5.0, while according to the experimental data maximum adsorbency was 11.0 g/g for logR_0 = 4.8 (Fig. 9.49).

Table 9.6 Coefficients of eq. (9.10)

T (°C)	i	a_{ij}	b_{ij}	R^2
160	WD	0.4738	0.8876	0.4861
180	WD	0.6018	0.6029	0.6902
200	WD	0.5295	0.8805	0.7575
240	WD	0.5929	0.4368	0.9535
160	WC	0.7509	0.2097	0.9400
180	WC	0.6096	0.9960	0.5357
200	WC	0.8138	0.0376	0.9339
240	WC	0.7868	0.1289	0.9878
All	WD	0.6107	0.3244	0.8957
All	WC	0.7594	0.2453	0.9594
All	CD	0.8109	0.0931	0.9494

ABS shows maximum diesel oil adsorbency value equal to 5.6 g/g at Severity Factor logR_0 = 5.0, while according to the experimental data maximum adsorbency was 6.9 g/g for logR_0 = 4.8 (Fig. 9.50).

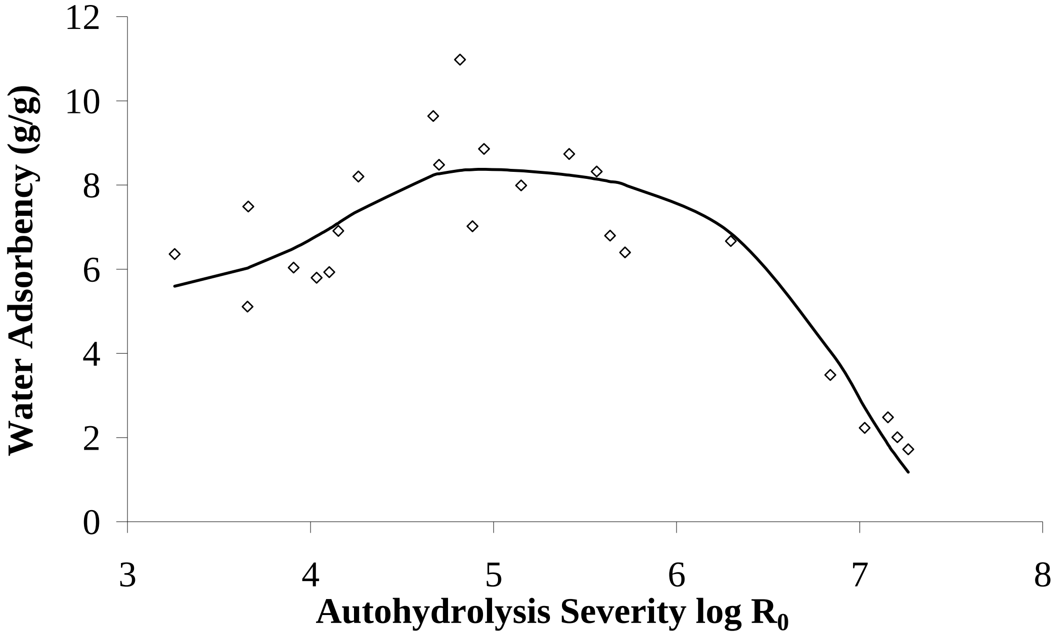


Fig. 9.49 ABS water adsorbency values vs. Severity Factor R_0

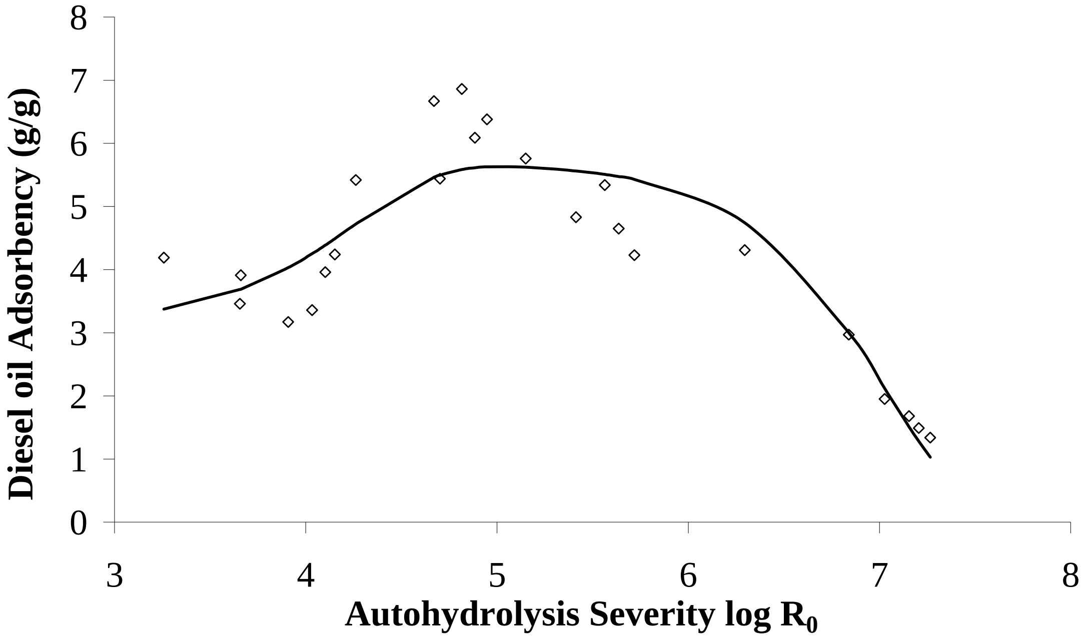


Fig. 9.50 ABS diesel oil adsorbency values vs. Severity Factor R_0

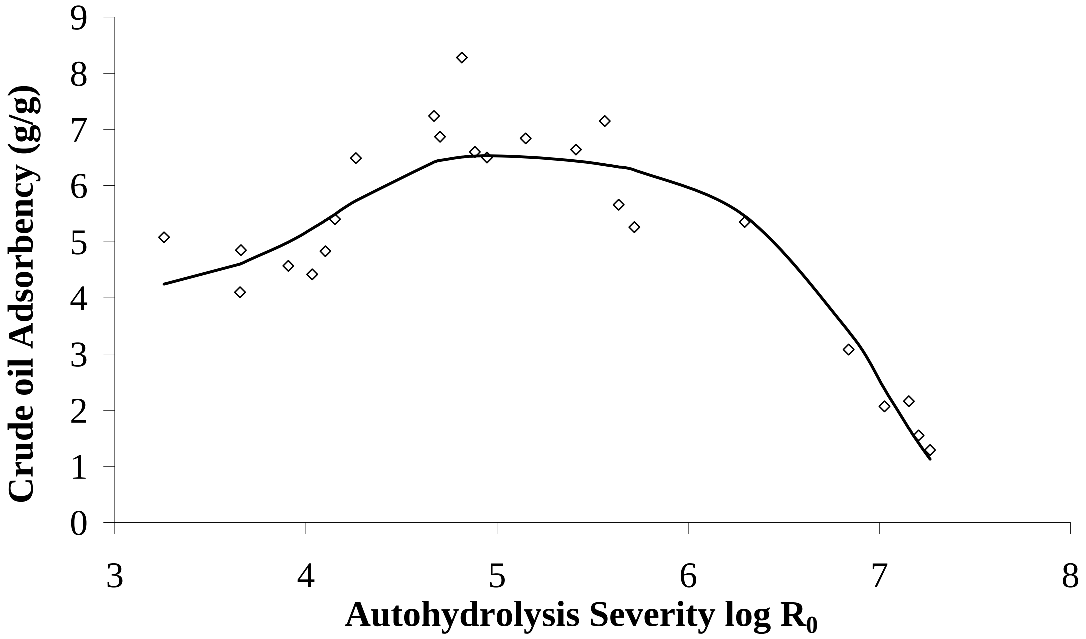


Fig. 9.51 ABS crude oil adsorbency values vs. Severity Factor R_0

ABS shows maximum crude oil adsorbency value equal to 6.5 g/g at Severity Factor $\log R_0$ = 5.0, while according to the experimental data maximum adsorbency was 8.3 g/g for $\log R_0$ = 4.8 (Fig. 9.51). The optimum experimental conditions for all the above mentioned cases are 180°C for 30-50 min.

9.6 Acid hydrolyzed barley straw adsorbencies

Pure liquids

Acid-hydrolyzed barley straw's adsorbency was examined by D.K. Sidiras, and I.G. Konstantinou, (2012), in the study "Modification of barley straw by acid hydrolysis to be used as diesel and crude adsorbent", which was presented in the 20th European Biomass Conference and Exhibition 2012, held in Milan.

The experimental results of the water and oil adsorbency of the untreated (UBS) and the acid hydrolyzed barley straw (AcBS) are shown in the following diagrams. Water adsorbency (Table 9.7, Fig. 9.52) was found to increase by increasing the acid hydrolysis time for reaction-ending temperatures 160-200^{o}C and to decrease at 220^{o}C. The maximum of water adsorbency value was 12.0 g/g at 160^{o}C for 40 min.

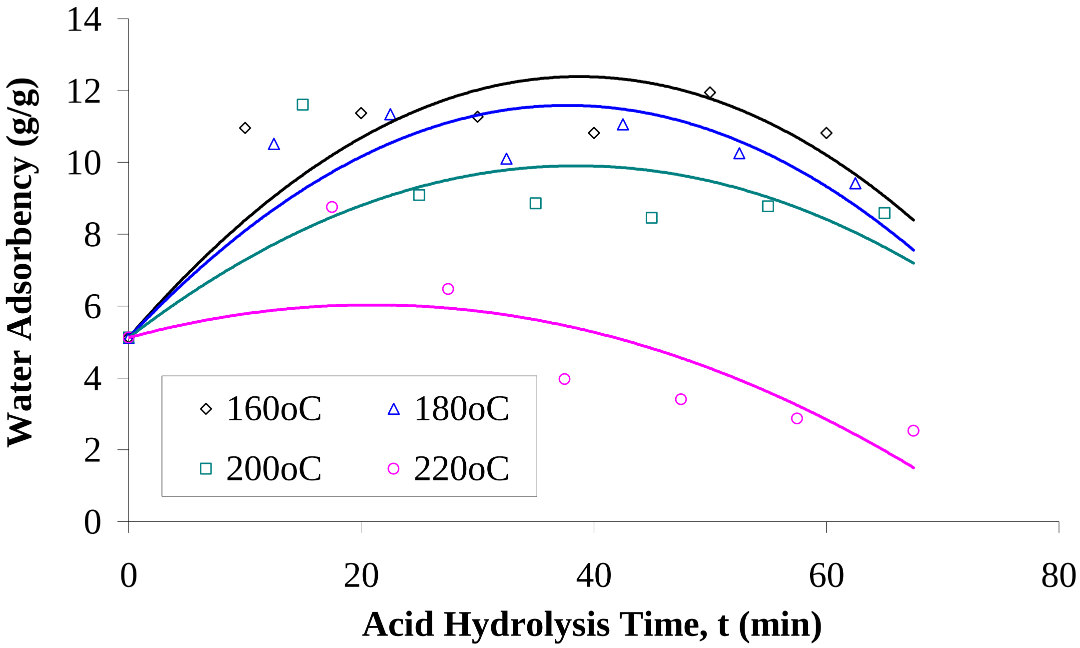


Fig. 9.52 UBS and AcBS water adsorbency values vs. the acid hydrolysis time

Similarly, diesel oil adsorbency (Table 9.7, Fig. 9.53) was found to increase by increasing the acid hydrolysis time for reaction-ending temperatures 160-200^{o}C and to decrease at 220^{o}C. The maximum of diesel oil adsorbency value was 6.7 g/g at 160^{o}C for 40 min.

Table 9.7 Water, diesel oil and crude oil adsorbency values of UBS and AcBS

		Water	Diesel oil	Crude oil
T (^{o}C)	t (min)	Adsorbency (g/g)		
Untreated		5.12	3.38	4.05
160	0	10.96	6.39	7.99
160	10	11.37	6.15	8.65
160	20	11.27	6.40	8.40
160	30	10.82	6.02	7.59
160	40	11.95	6.74	8.64
160	50	10.82	4.89	5.94
180	0	10.52	5.89	8.13
180	10	11.34	5.96	7.45
180	20	10.10	5.14	6.44
180	30	11.06	4.99	6.20
180	40	10.26	5.10	7.17
180	50	9.42	5.16	6.68
200	0	11.60	4.69	5.96
200	10	9.09	4.94	6.08
200	20	8.86	5.23	7.28
200	30	8.45	5.37	6.58
200	40	8.78	5.45	6.13
200	50	8.59	4.78	5.40
220	0	8.76	6.65	7.26
220	10	6.47	4.20	4.94
220	20	3.97	3.84	4.24
220	30	3.40	2.47	3.51
220	40	2.87	2.87	2.98
220	50	2.53	2.32	3.60

Finally, crude oil adsorbency (Table 9.7, Fig. 9.54) was found to increase by increasing the acid hydrolysis time for reaction-ending temperatures 160-220^{o}C.

The maximum of crude oil adsorbency value was 8.7 g/g at 160^{o}C for 10 min. The water, diesel oil and crude oil adsorbency can be given as function of the acid hydrolysis time as follows:

$$A_i = a_i t^2 + b_i t + c_i \tag{9.11}$$

where: A is the adsorbency (g/g), t is the acid-hydrolysis time (min), and i=W, D, C; W is for Water, D is for Diesel oil and C is for Crude oil. The values of the coefficients of eq. (9.11) are given in Table 9.8.

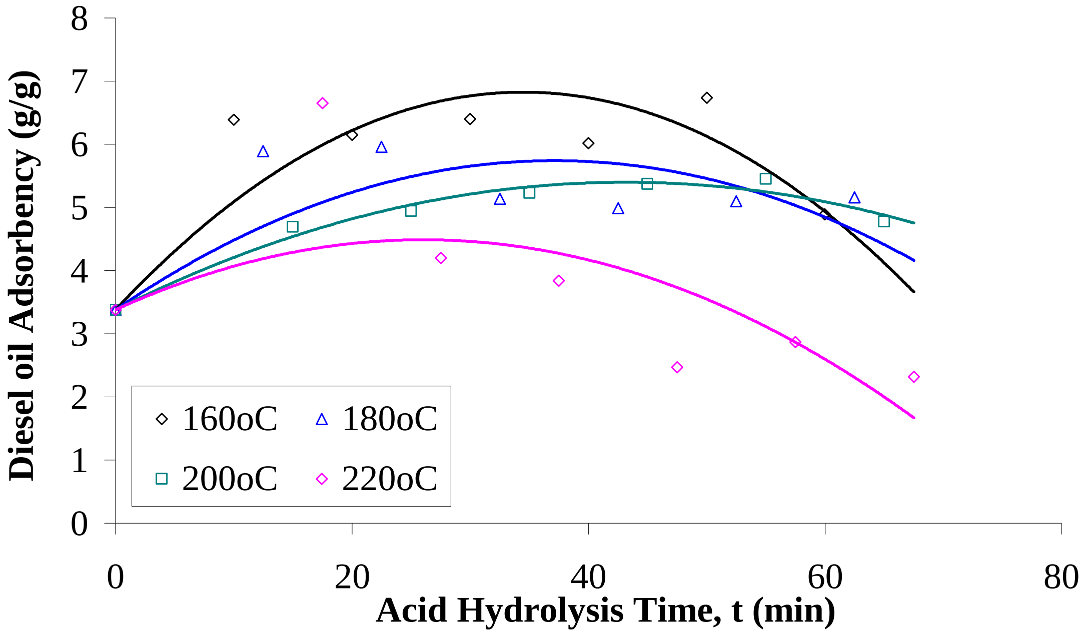


Fig. 9.53 UBS and AcBS diesel oil adsorbency values vs. the acid hydrolysis time

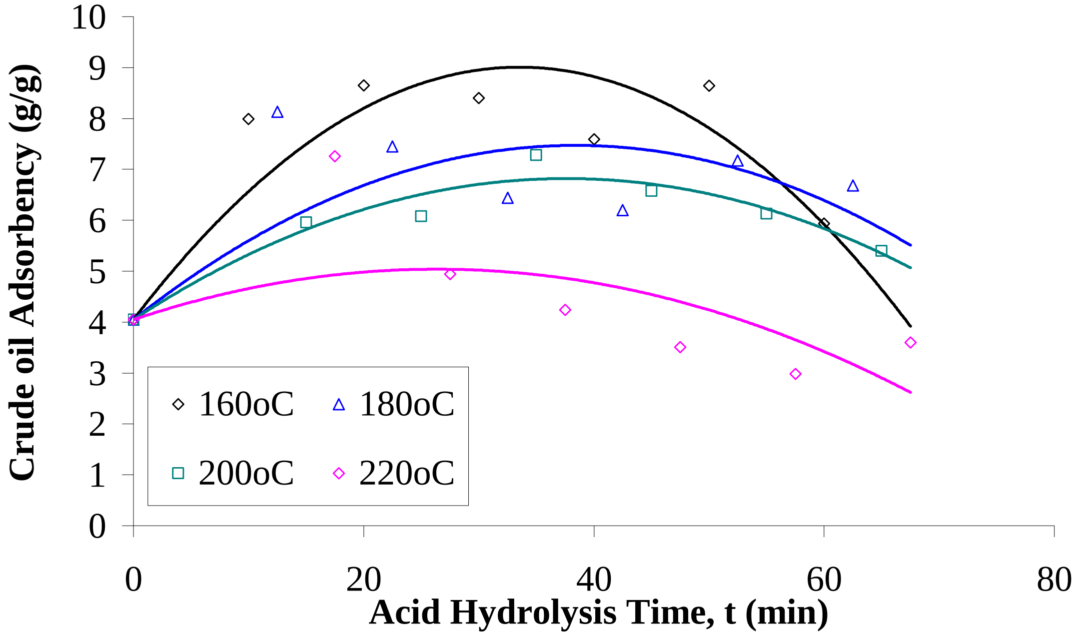


Fig. 9.54 UBS and AcBS crude oil adsorbency values vs. the acid hydrolysis time

Diesel oil and crude oil adsorbency was found to increase linearly by increasing the water adsorbency (Figs 9.55 and 9.56). Moreover, crude oil adsorbency was found to increase linearly by increasing the diesel oil adsorbency (Fig. 9.57).

Table 9.8 Coefficients of eq. (9.11)

T (°C)	i	a_i	b_i	c_i	R^2
160	W	-0.0048	0.3750	5.12	0.6783
180	W	-0.0045	0.3429	5.12	0.7564
200	W	-0.0032	0.2486	5.12	0.2609
220	W	-0.0021	0.0873	5.12	0.5811
160	D	-0.0029	0.1999	3.38	0.6753
180	D	-0.0017	0.1271	3.38	0.3333
200	D	-0.0011	0.0936	3.38	0.9682
220	D	-0.0016	0.0852	3.38	0.4320
160	C	-0.0044	0.2958	4.05	0.7335
180	C	-0.0023	0.1782	4.05	0.2081
200	C	-0.0020	0.1474	4.05	0.9253
220	C	-0.0014	0.0752	4.05	0.3336

The AcBS water and diesel oil adsorbency values, for both simulation model and experimental data, increase from 5.1 g/g to approximately 11-12 g/g (Fig. 9.58) and from 3.4 g/g to 5.8 g/g (Fig. 9.59), respectively, at the mildest conditions used here in (160°C for 0 min).

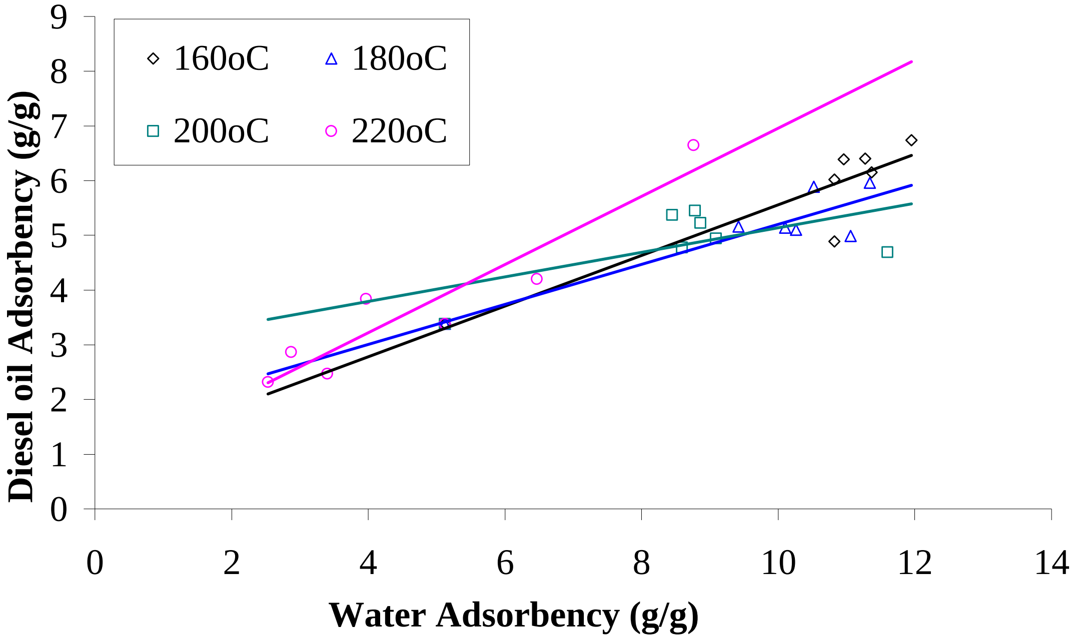


Fig. 9.55 UBS and AcBS diesel oil adsorbency values vs. water adsorbency values

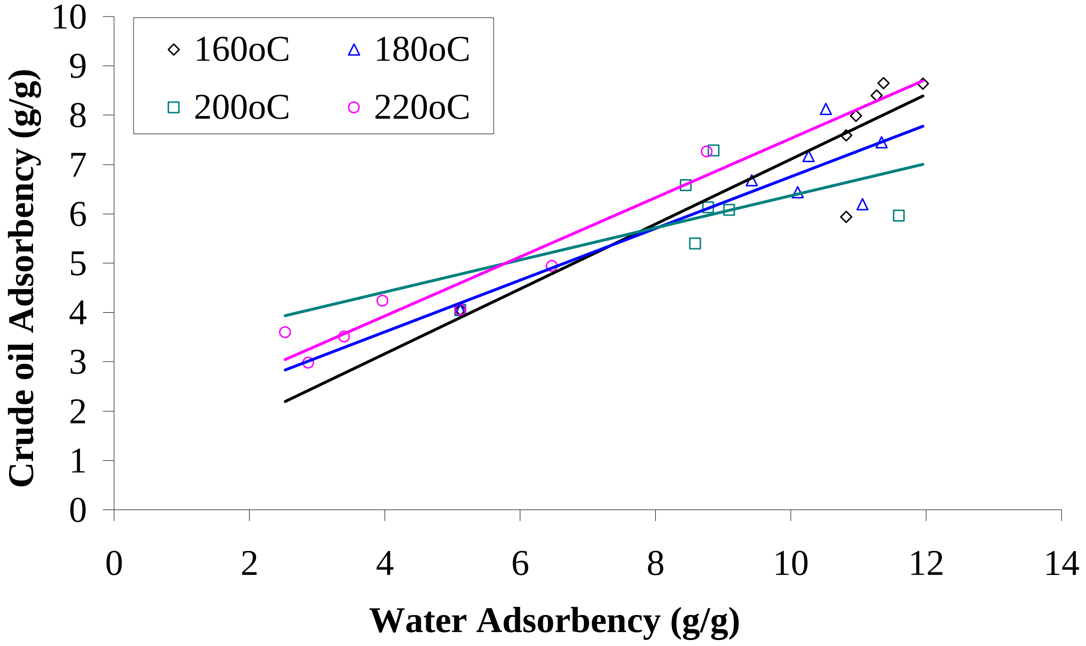


Fig. 9.56 UBS and AcBS crude oil adsorbency values vs. water adsorbency values

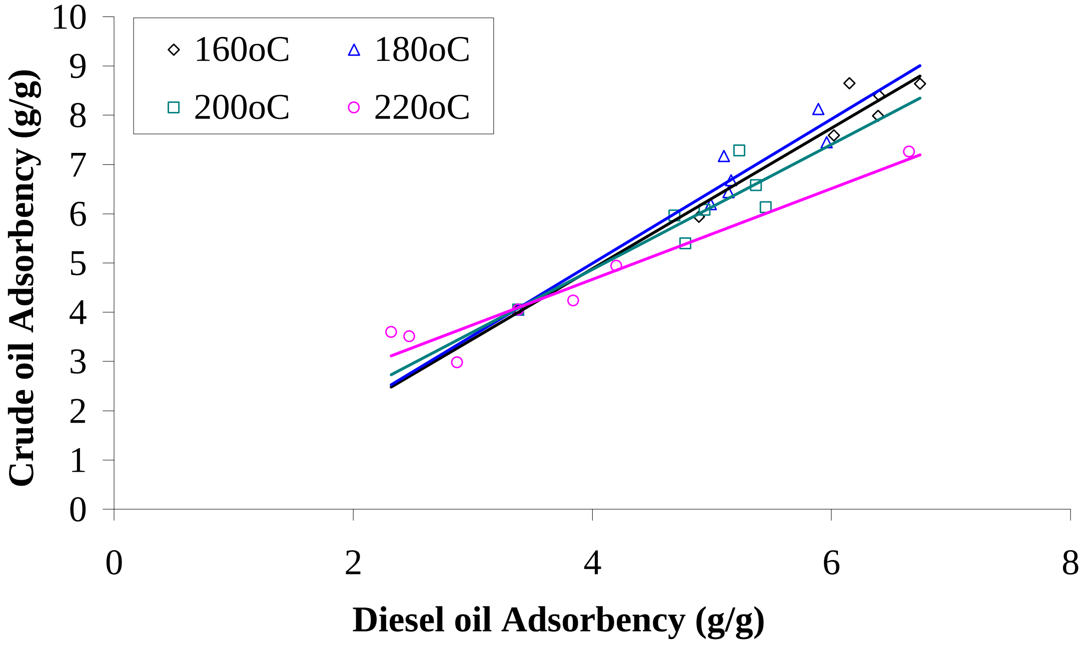


Fig. 9.57 UBS and AcBS crude oil adsorbency vs. diesel oil adsorbency values

AcBS shows maximum crude oil adsorbency value equal to 7.2 g/g at Severity Factor $\log R_0 = 4.3$ (Fig. 9.60). According to the simulation model maximum crude oil adsorbency value was 7.2 g/g for $\log R_0 = 4.3$ (i.e., 180°C for 10 min), while according to the experimental data maximum adsorbency was 8.7 g/g for $\log R_0 = 3.7$ (i.e., 160°C for 10 min).

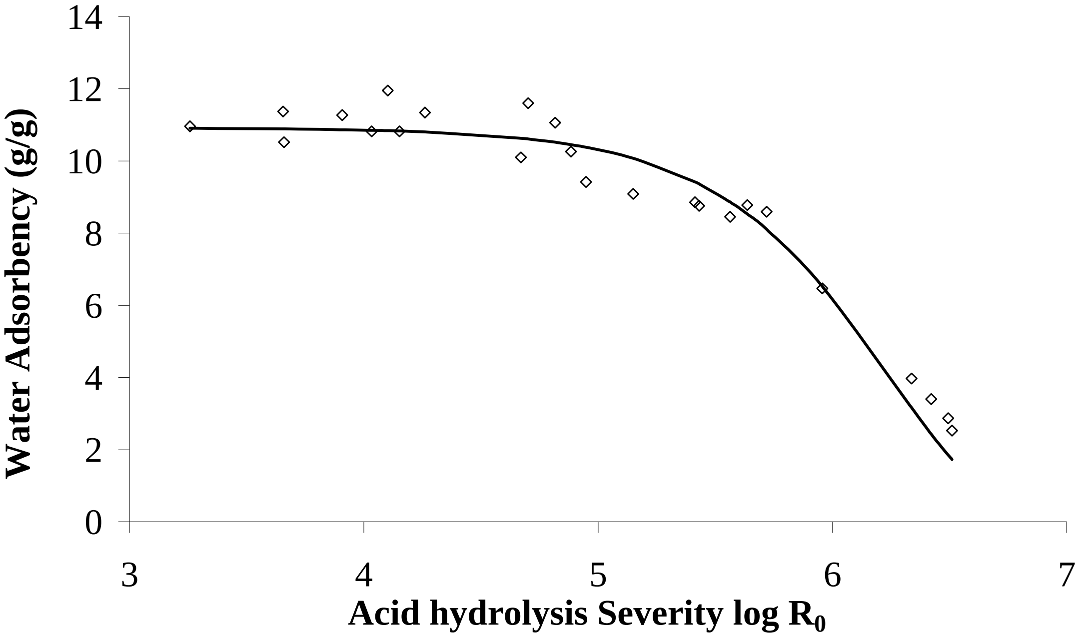


Fig. 9.58 AcBS water adsorbency values vs. Severity Factor R_0

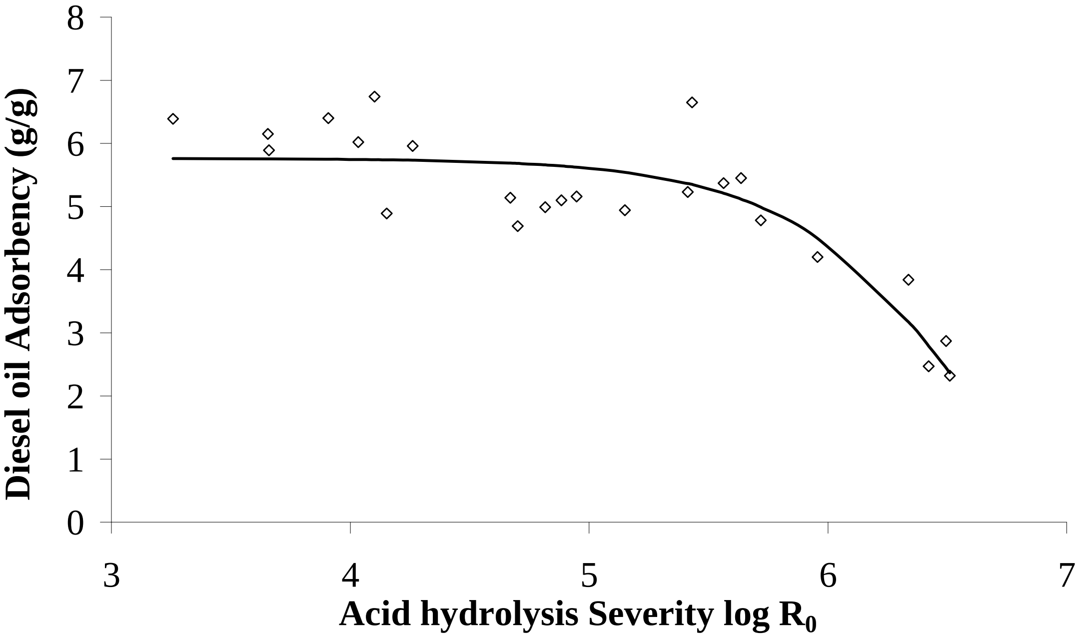


Fig. 9.59 AcBS diesel oil adsorbency values vs. Severity Factor R_0

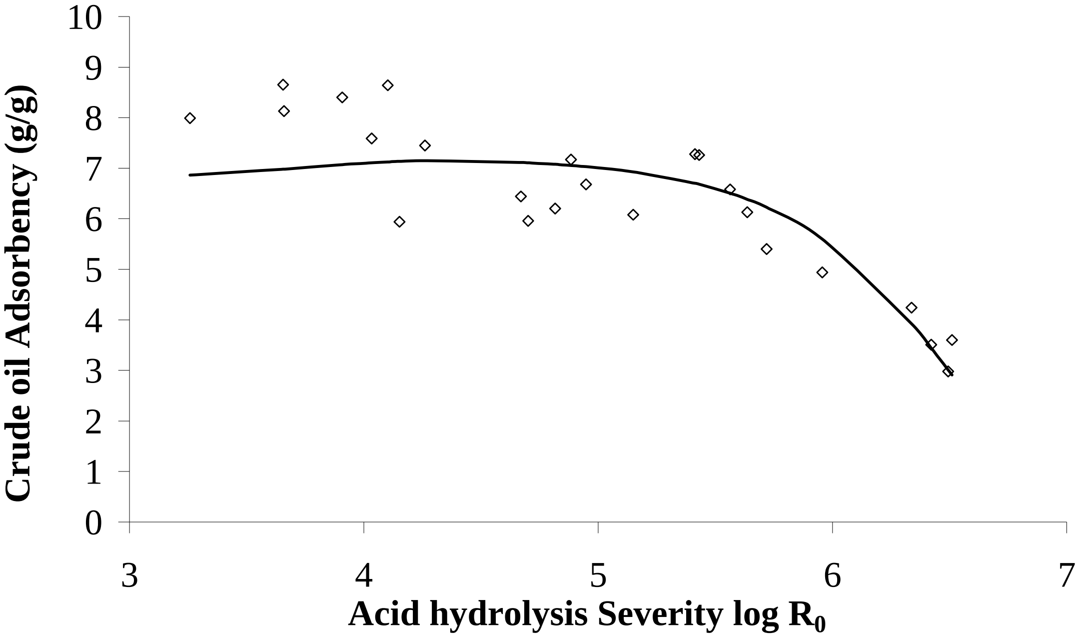


Fig. 9.60 AcBS crude oil adsorbency values vs. Severity Factor R_0

9.7 Straw's adsorptivity comparisons

In this section, water adsorbency and oil adsorbency (diesel oil and crude oil) of wheat straw (AWS and AcWS) and barley straw (ABS and AcBS), on pure liquids, were thoroughly compared in order to display the differences between the different straw (wheat and barley) and the different treatment (auto-hydrolysis and acid hydrolysis).

Furthermore, the adsorption capacity of wheat straw (AWS) in the cases of DOS and COS on: freshwater, seawater and substitute seawater was compared in order to determine the differences.

Comparison between AWS and AcWS adsorbencies on pure liquids

In this sub-chapter, the adsorption capacity of wheat straw on pure liquids (water, diesel oil and crude oil) in the cases of AWS and AcWS was compared in order to find the differences. The differences of the water, diesel oil and crude oil adsorbencies for AWS and AcWS are shown in the following Figs. 9.61, 9.62 and 9.63.

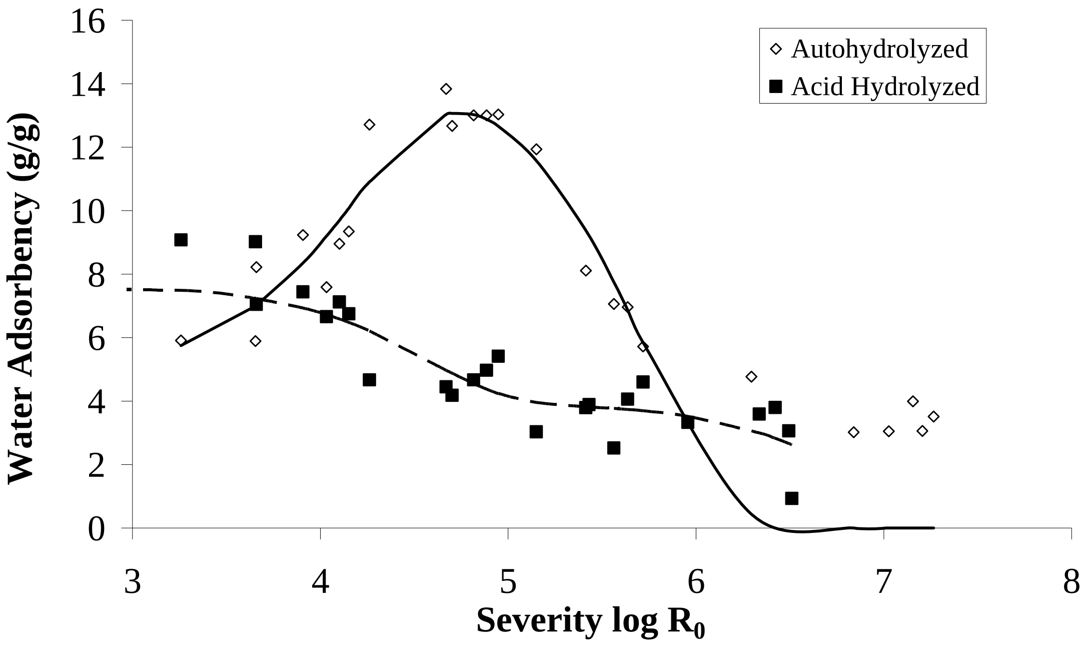


Fig. 9.61 Water adsorbency values vs. Severity Factor R_0 for AWS and AcWS

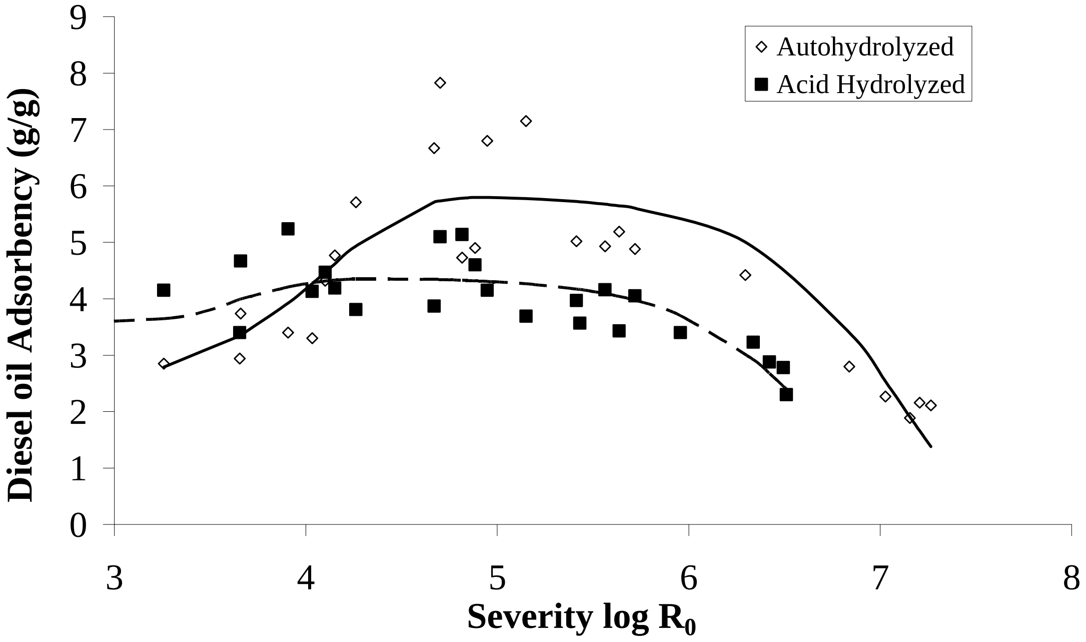


Fig. 9.62 Diesel oil adsorbency values vs. Severity Factor R_0 for AWS and AcWS

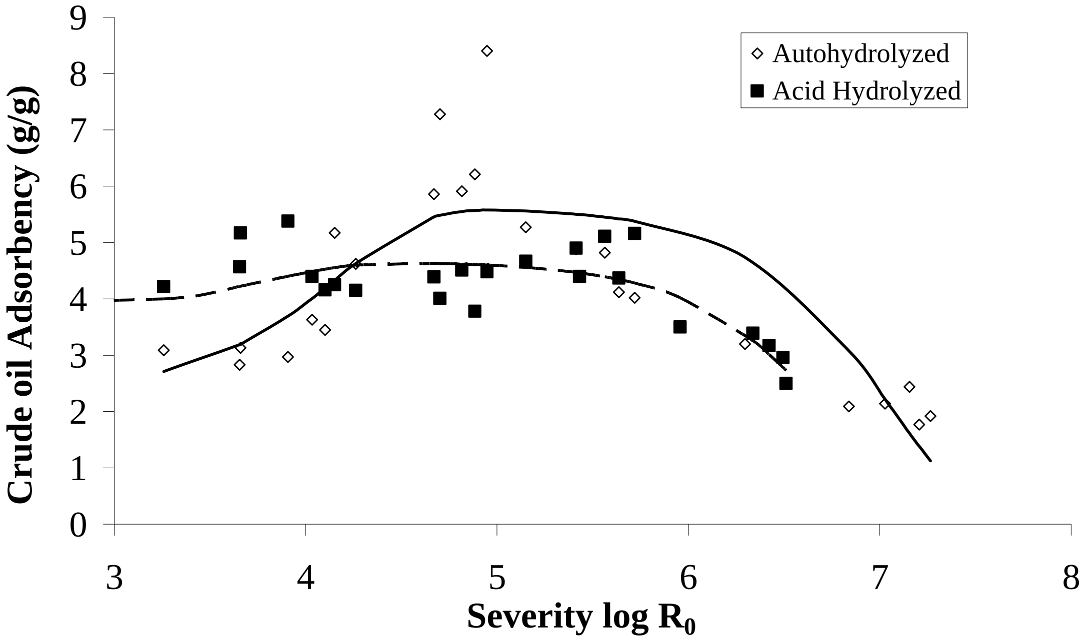


Fig. 9.63 Crude oil adsorbency values vs. Severity Factor R_0 for AWS and AcWS

Comparison between ABS and AcBS adsorbencies on pure liquids

In this sub-chapter, the adsorption capacity of barley straw on pure liquids (water, diesel oil and crude oil) in the cases of ABS and AcBS was compared in order to find the differences. The differences of the water, diesel oil and crude oil adsorbencies for ABS and AcBS are shown in the following Figs. 9.64, 9.65 and 9.66.

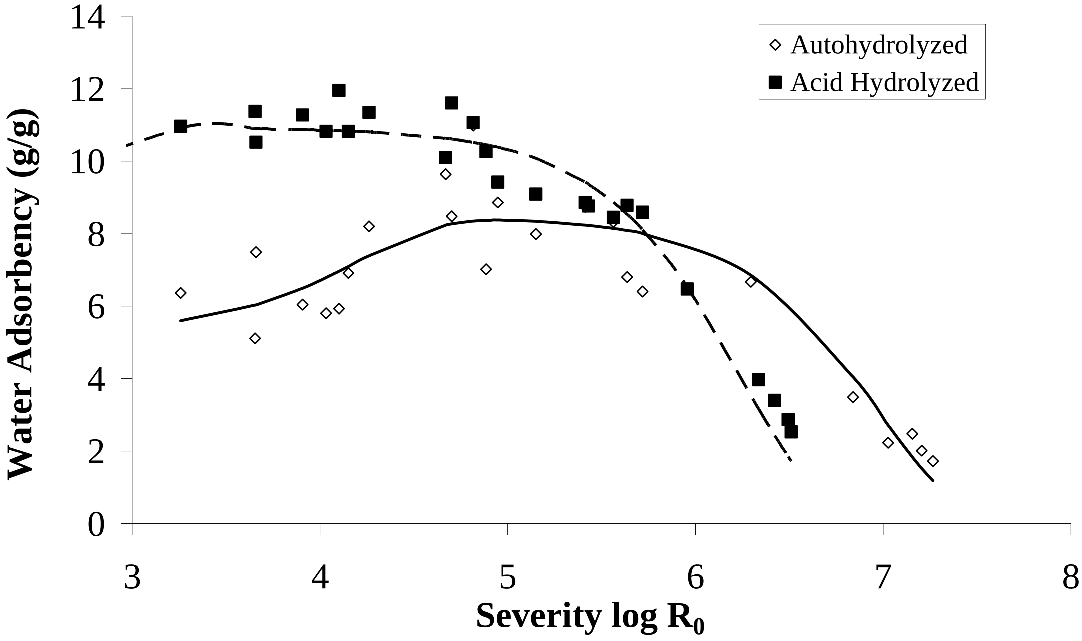


Fig. 9.64 Water adsorbency values vs. Severity Factor R_0 for ABS and AcBS

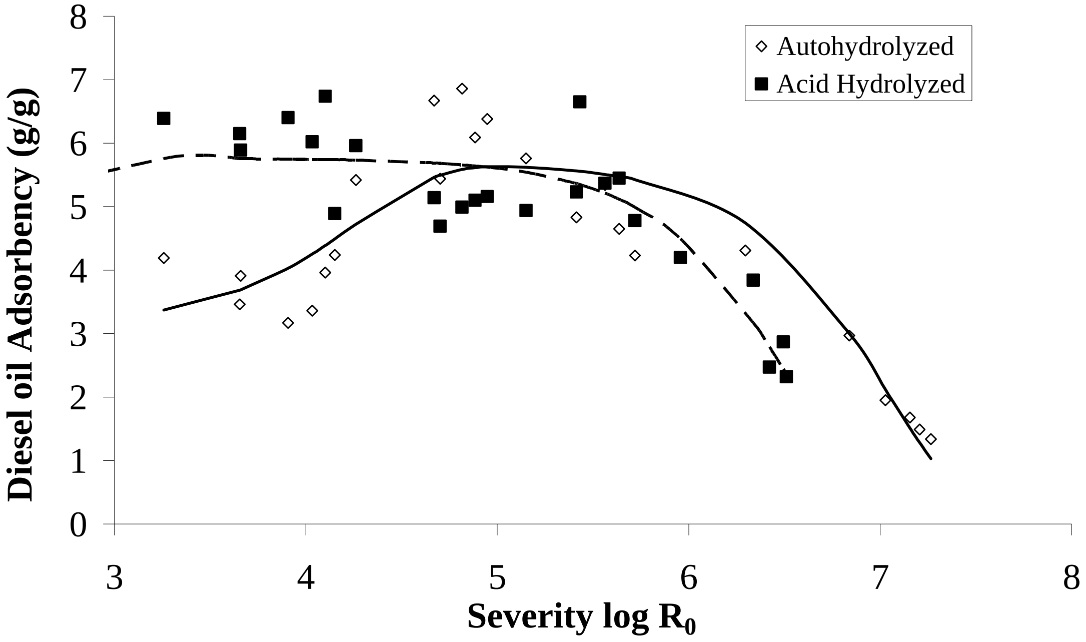


Fig. 9.65 Diesel oil adsorbency values vs. Severity Factor R_0 for ABS and AcBS

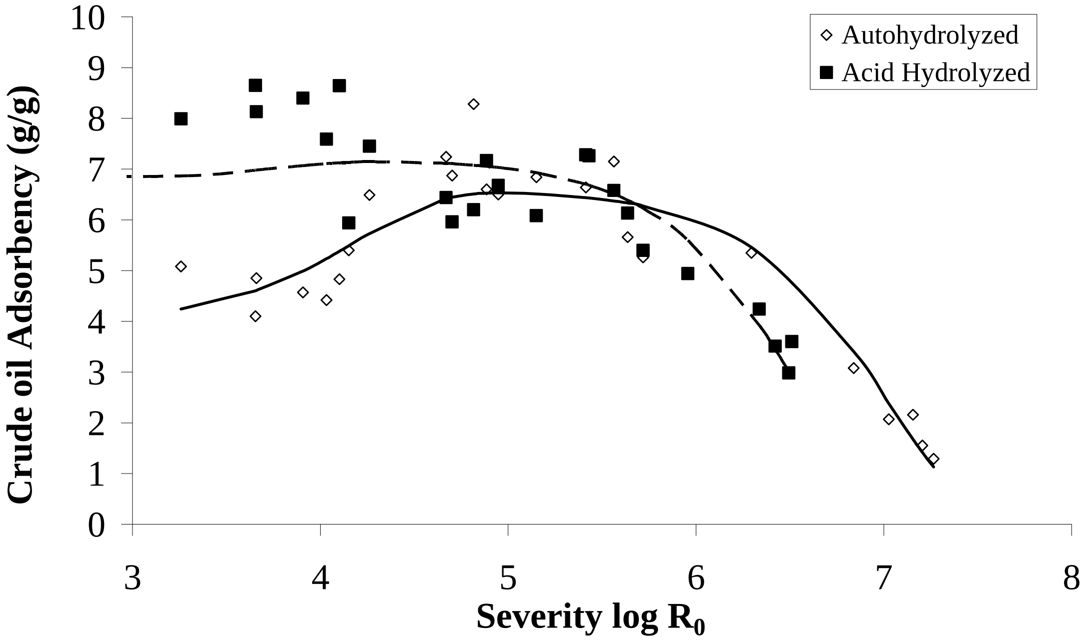


Fig. 9.66 Crude oil adsorbency values vs. Severity Factor R_0 for ABS and AcBS

Comparison between AWS and ABS adsorbencies on pure liquids

In this sub-chapter, the adsorption capacity of straw on pure liquids (water, diesel oil and crude oil) in the cases of AWS and ABS was compared in order to find the differences. The differences of the water, diesel oil and crude oil adsorbencies for AWS and ABS are shown in Figs. 9.67, 9.68 and 9.69.

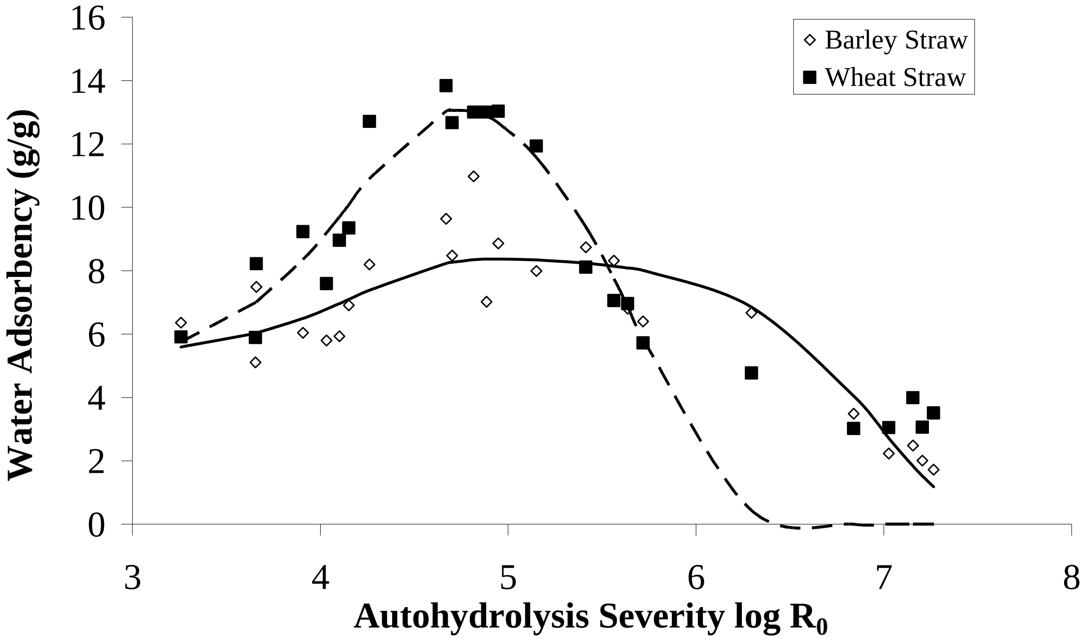


Fig. 9.67 Water adsorbency values vs. Severity Factor R_0 for AWS and ABS

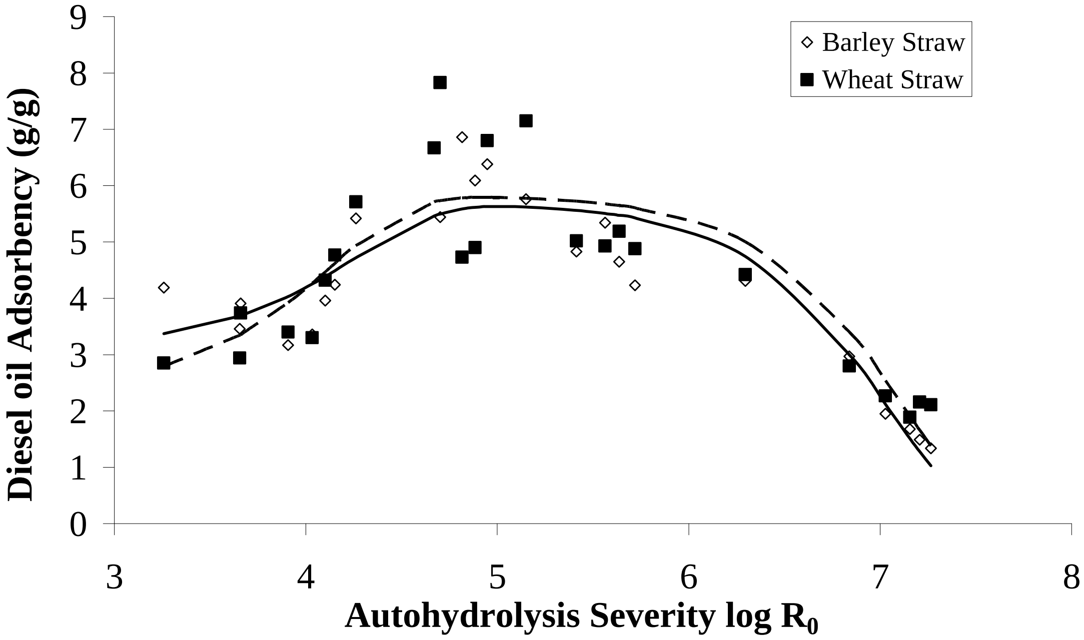


Fig. 9.68 Diesel oil adsorbency values vs. Severity Factor R_0 for AWS and ABS

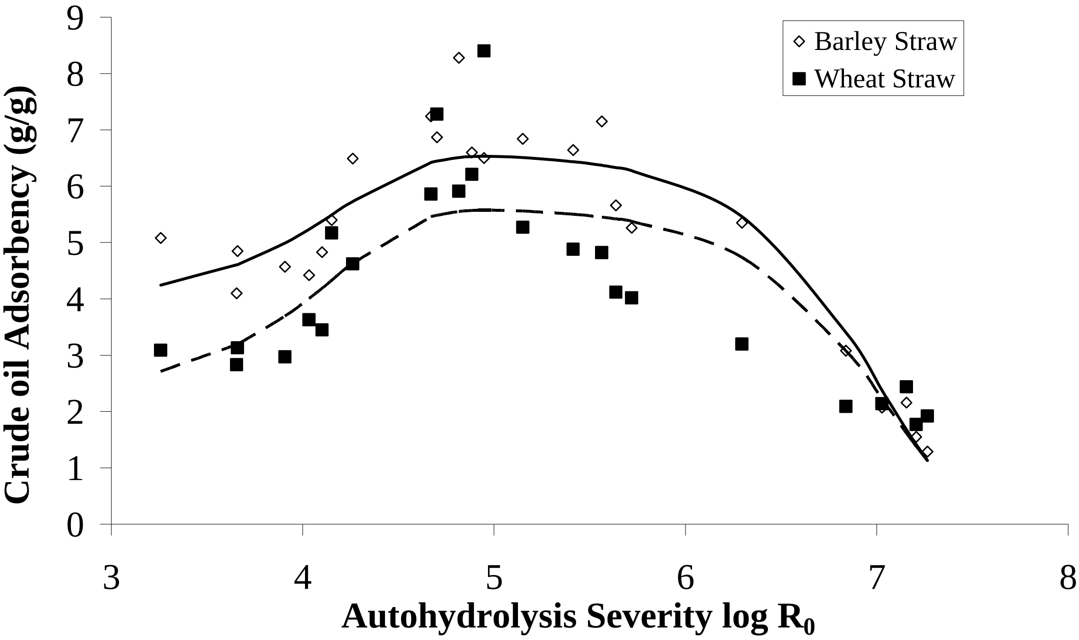


Fig. 9.69 Crude oil adsorbency values vs. Severity Factor R_0 for AWS and ABS

Comparison between AcWS and AcBS adsorbencies on pure liquids

In this sub-chapter, the adsorption capacity of straw on pure liquids (water, diesel oil and crude oil) in the cases of AcWS and AcBS was compared in order to find the differences.

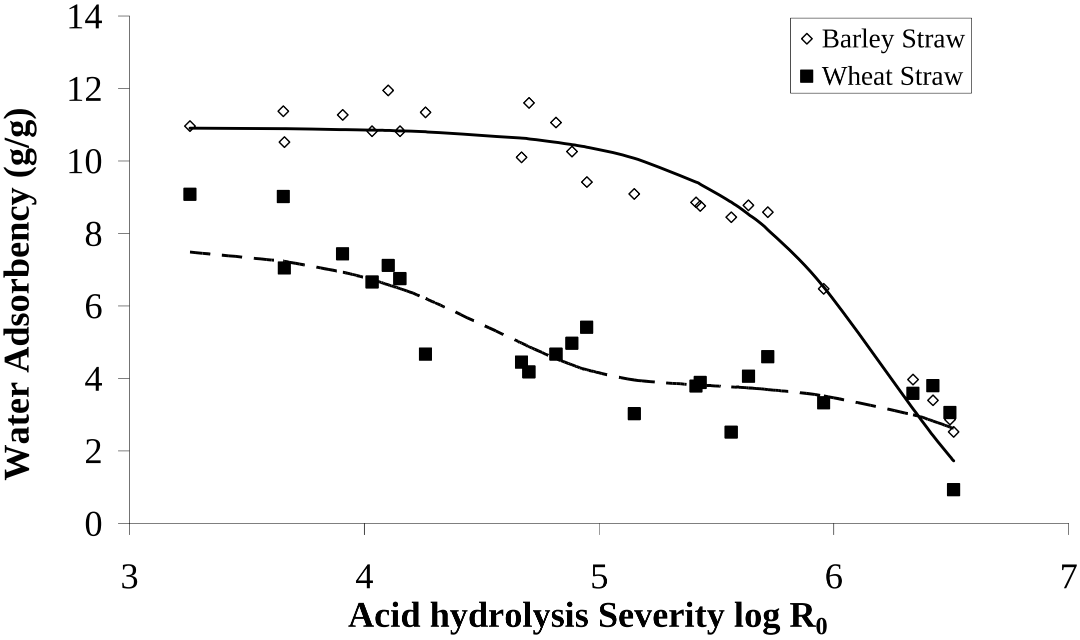


Fig. 9.70 Water adsorbency values vs. Severity Factor R_0 for AcWS and AcBS

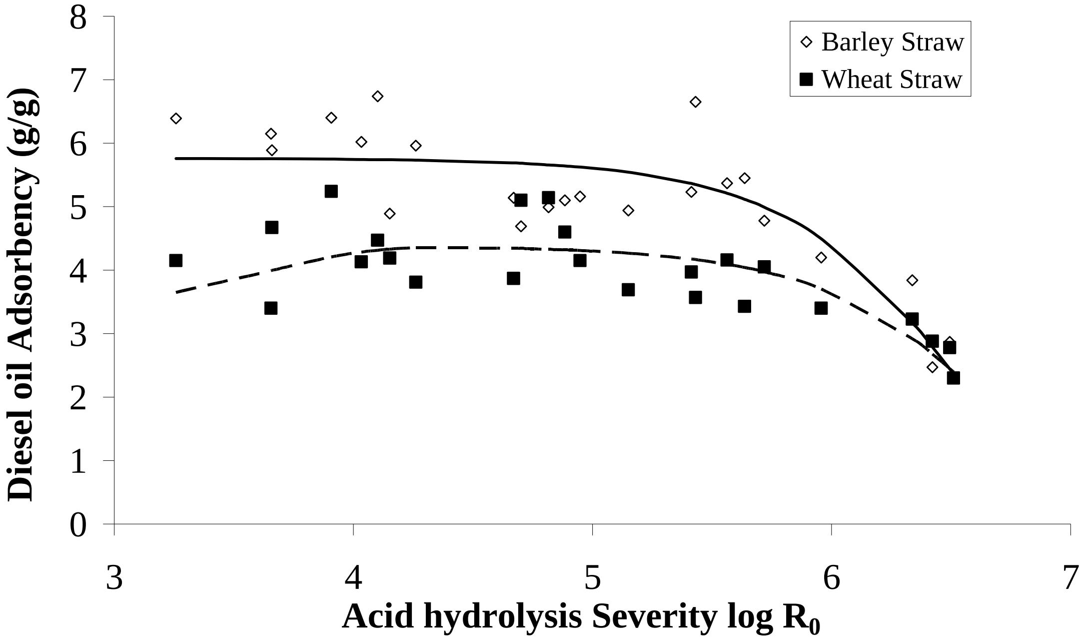


Fig. 9.71 Diesel oil adsorbency values vs. Severity Factor R_0 for AcWS and AcBS

The differences of the water, diesel oil and crude oil adsorbencies for AcWS and AcBS are shown in Figs. 9.70, 9.71 and 9.72.

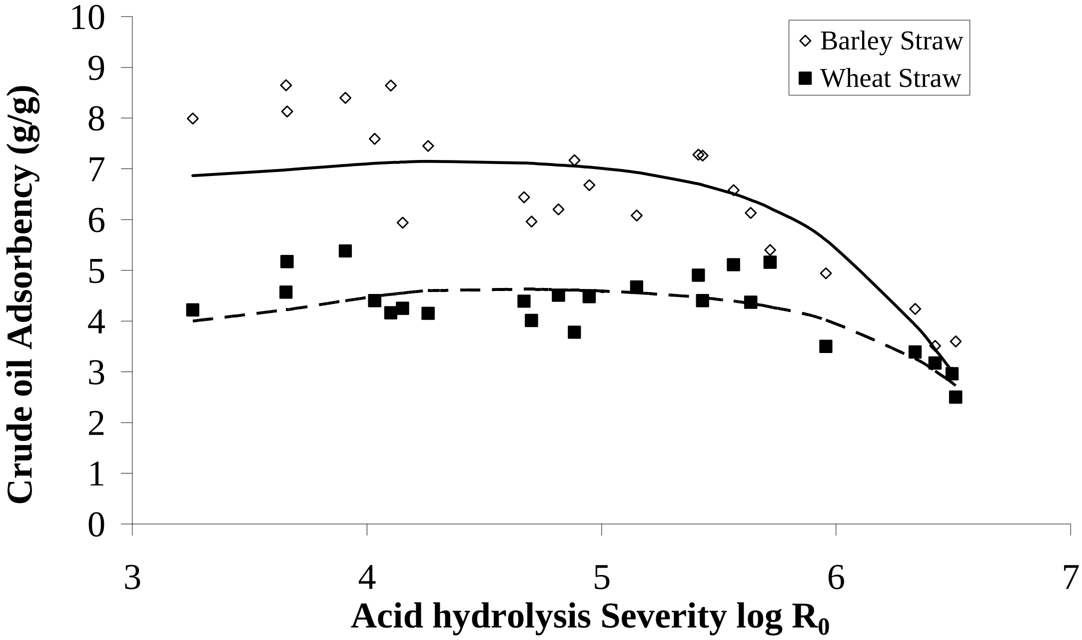


Fig. 9.72 Crude oil adsorbency values vs. Severity Factor R_0 for AcWS and AcBS

Water adsorbency values for AWS were higher than those of AcWS at the range of maximum adsorbencies values (Fig. 9.61). Diesel oil and crude oil adsorbencies values for AWS were higher than those of AcWS for $\log R_0 > 4.3$ (Figs. 9.62 and 9.63).

Water adsorbency values for ABS were higher comparing to AcBS values for $\log R_0 < 5.7$ (Fig. 9.64). Diesel oil adsorbency values for ABS were higher comparing to AcBS values for $\log R_0 < 4.9$ (Fig. 9.65), while, crude oil adsorbency values for ABS were higher than those of AcBS for $\log R_0 < 5.6$ (Fig. 9.66).

Water adsorbency values for AWS were higher than those of ABS values for $\log R_0 < 5.5$ (Fig. 9.67). Diesel oil adsorbency values for AWS were similar comparing to those of ABS values (Fig. 9.68), while, crude oil adsorbency values for AWS were higher than those of ABS (Fig. 9.69).

Finally, water, diesel oil and crude oil adsorbency values for AcBS were higher than those of AcWS values (Figs. 9.70, 9.71 and 9.72).

Comparison of UWS and AWS adsorbencies among DOS and COS on freshwater, seawater and substitute seawater

In this sub-chapter, the adsorption capacity of wheat straw in the cases of DOS and COS on: freshwater, seawater and substitute seawater was compared in order to determine the differences.

The UWS and AWS at optimal conditions (180 ^{o}C for 50 min reaction time) in the above mentioned conditions were examined as regards their adsorption capacities. Then statistical analysis, taking into account the experimental error resulting from the repeatability measurements, was done.

Finally, the results were thoroughly compared, to find out the differences among the three kinds of water in the DOS and COS mixtures on the adsorption capacity of the straw.

AWS water adsorbency value (Fig. 9.73) is higher for the case of DOS on substitute seawater and lower for the same case on seawater compared to the value corresponding to the same case on freshwater. UWS water adsorbency value is higher for the case of DOS on freshwater and lower for the same case on seawater compared to the value corresponding to the same case on substitute seawater.

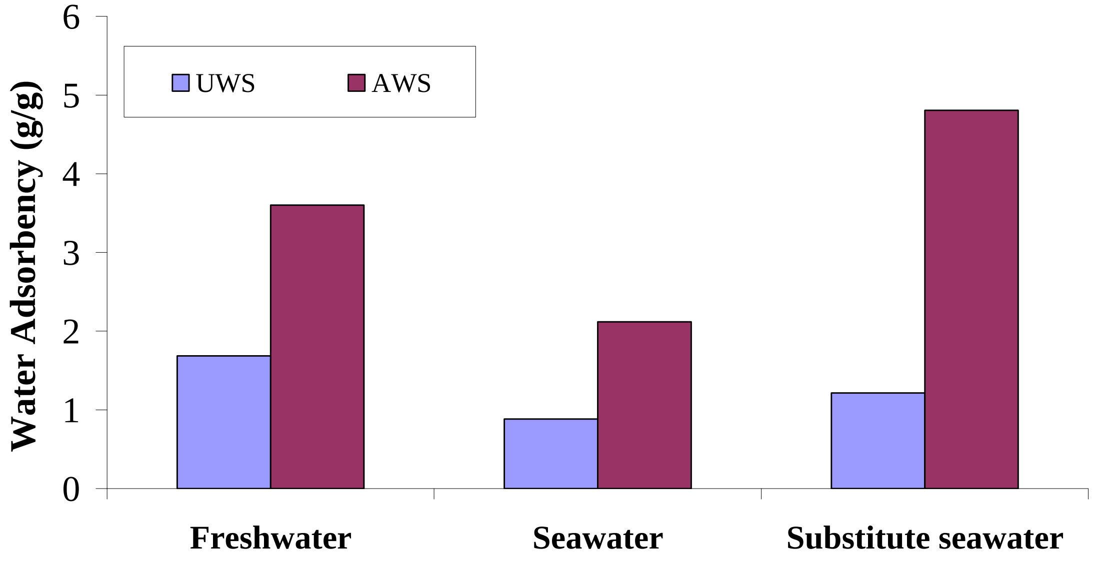


Fig. 9.73 UWS and AWS water adsorbency values for DOS on freshwater, seawater and substitute seawater

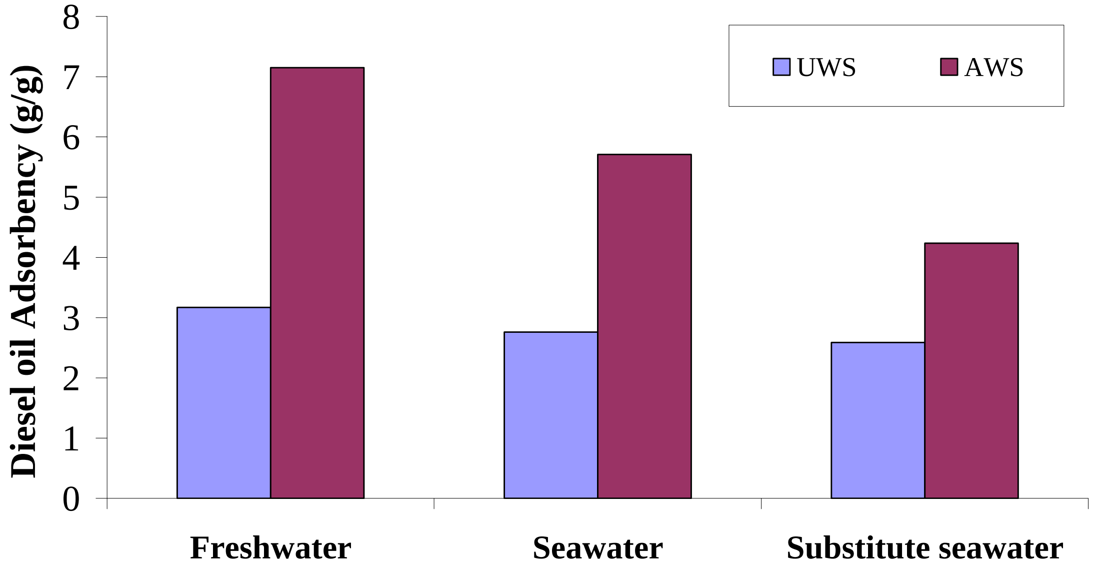


Fig. 9.74 UWS and AWS diesel oil adsorbency values for DOS on freshwater, seawater and substitute seawater

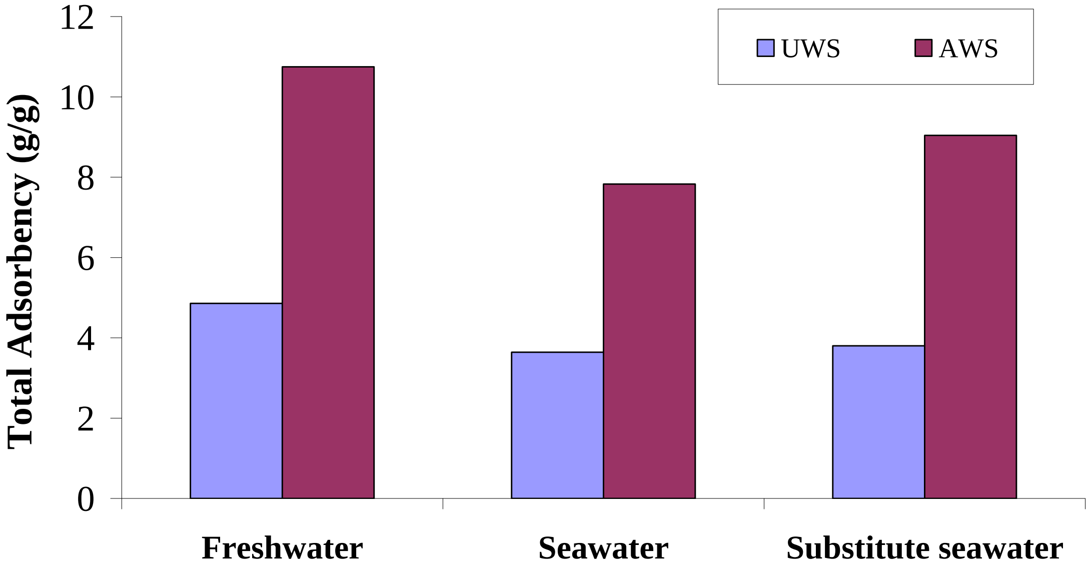


Fig. 9.75 UWS and AWS total adsorbency values for DOS on freshwater, seawater and substitute seawater

In all these cases AWS water adsorbency values are significantly higher (114-296%) than the relevant UWS water adsorbency values.

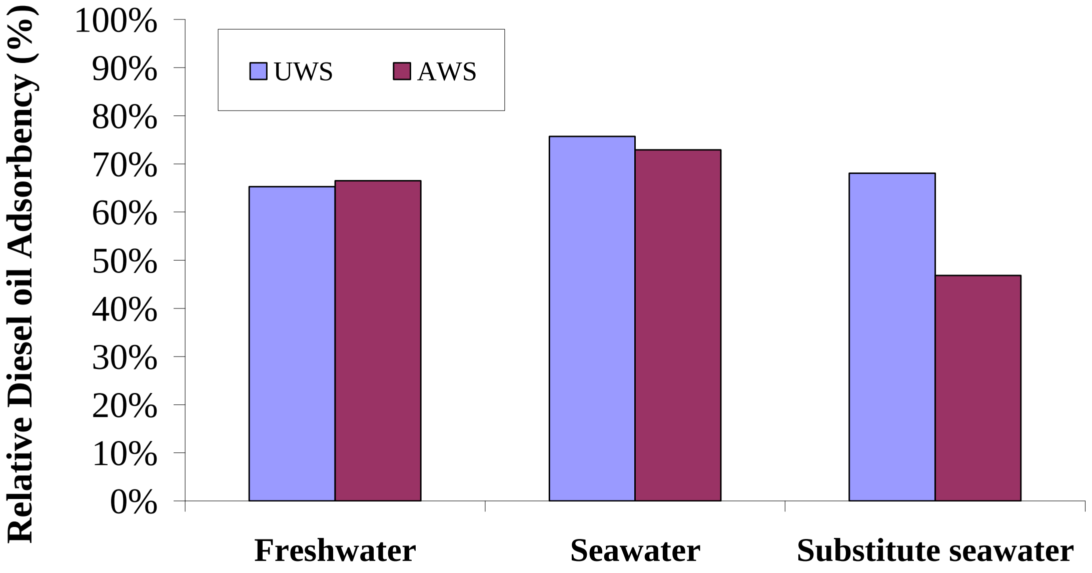


Fig. 9.76 UWS and AWS RDA values for DOS on freshwater, seawater and substitute seawater

AWS diesel oil adsorbency value (Fig. 9.74) is higher for the case of DOS on freshwater and lower for the same case on substitute seawater compared to the value corresponding to the same case on seawater. UWS diesel oil adsorbency value isn't significantly different among the cases of DOS on freshwater, seawater and substitute seawater. In all these cases AWS diesel oil adsorbency values are significantly higher (64-126%) than the relevant UWS diesel oil adsorbency values.

AWS total adsorbency value (Fig. 9.75) is higher for the case of DOS on freshwater and lower for the same case on seawater compared to the value corresponding to the same case on substitute seawater. UWS total adsorbency value isn't significantly different among the cases of DOS on freshwater, seawater and substitute seawater. In all these cases AWS total adsorbency values are significantly higher (115-138%) than the relevant UWS total adsorbency values.

AWS RDA value (Fig. 9.76) is higher for the case of DOS on seawater and lower for the same case on substitute seawater compared to the value corresponding to the same case on freshwater. UWS RDA value isn't significantly different among the cases of DOS on freshwater, seawater and substitute seawater. In all these cases AWS RDA values aren't significantly different compared to the relevant UWS RDA values.

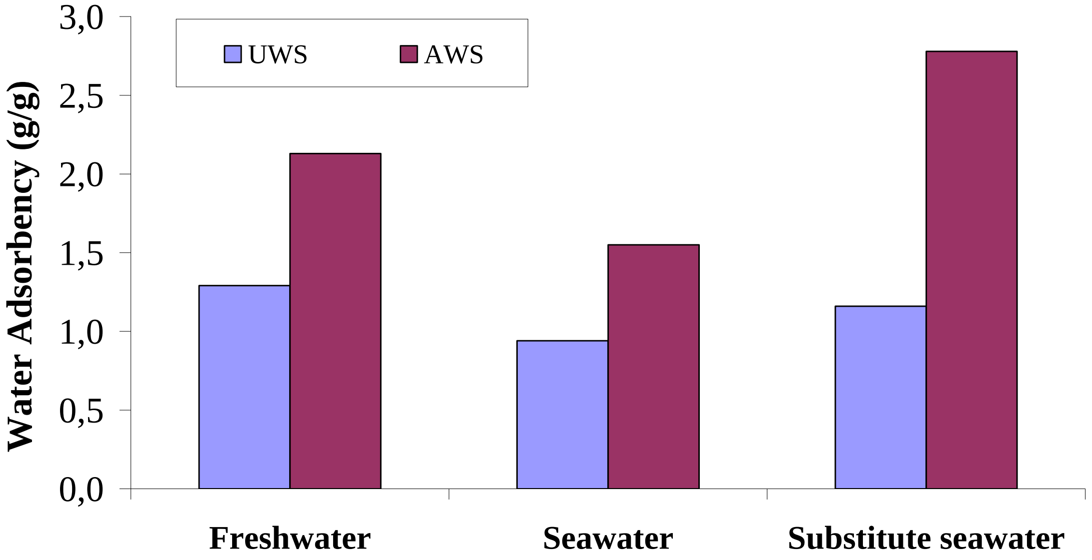


Fig. 9.77 UWS and AWS water adsorbency values for COS on freshwater, seawater and substitute seawater

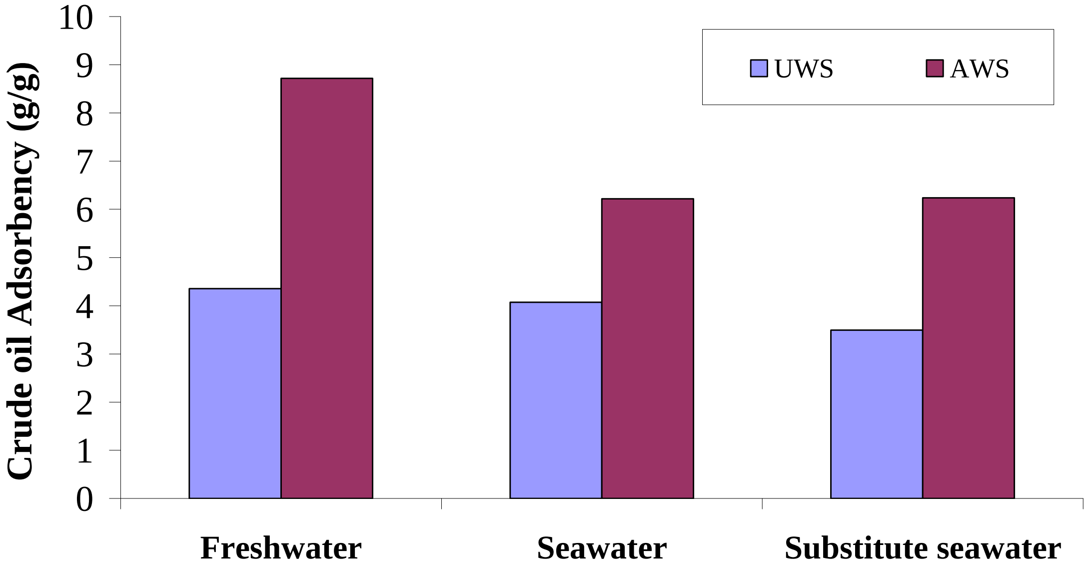


Fig. 9.78 UWS and AWS crude oil adsorbency values for COS on freshwater, seawater and substitute seawater

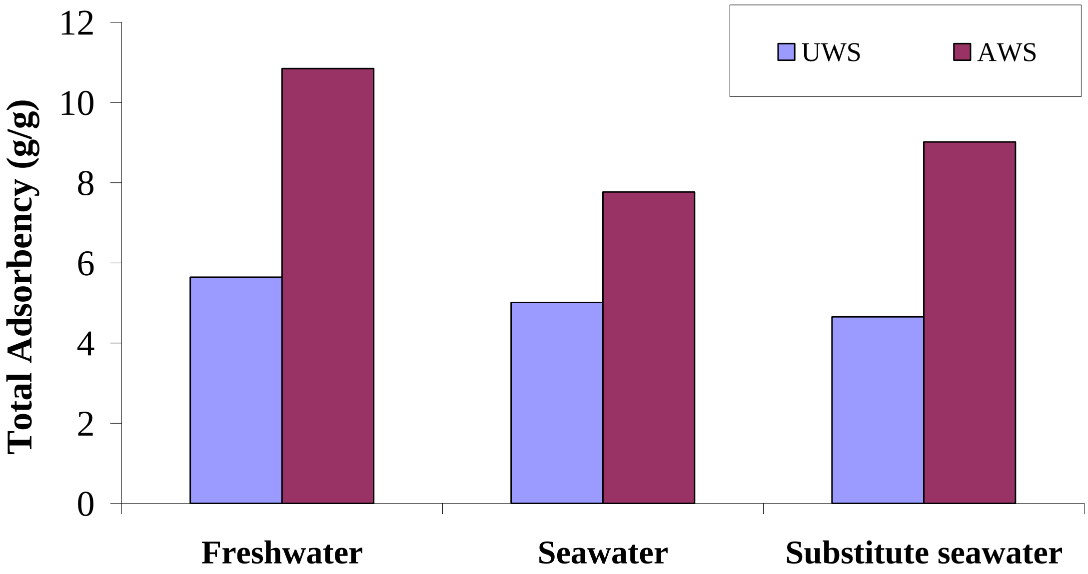


Fig. 9.79 UWS and AWS total adsorbency values for COS on freshwater, seawater and substitute seawater

AWS water adsorbency value (Fig. 9.77) is higher for the case of COS on substitute seawater and lower for the same case on seawater compared to the value corresponding to the same case on freshwater. UWS water adsorbency value isn't significantly different among the cases of COS on freshwater, seawater and substitute seawater. In all these cases AWS water adsorbency values are significantly higher (65-140%) than the relevant UWS water adsorbency values.

AWS crude oil adsorbency value (Fig. 9.78) is higher for the case of COS on freshwater compared to the values corresponding to the same case on seawater and on substitute seawater. UWS crude oil adsorbency value isn't significantly different among the cases of COS on freshwater, seawater and substitute seawater. In all these cases AWS crude oil adsorbency values are significantly higher (53-100%) than the relevant UWS crude oil adsorbency values.

AWS total adsorbency value (Fig. 9.79) is higher for the case of COS on freshwater compared to the values corresponding to the same case on seawater and on substitute seawater. UWS total adsorbency value isn't significantly different among the cases of COS on freshwater, seawater and substitute seawater. In all these cases AWS total adsorbency values are significantly higher (55-94%) than the relevant UWS total adsorbency values.

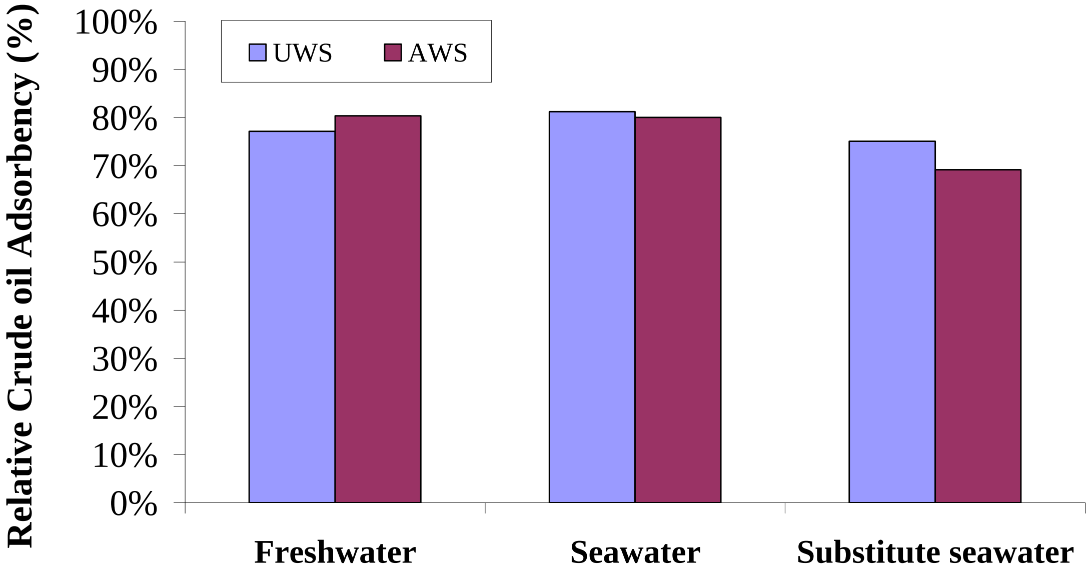


Fig. 9.80 UWS and AWS RCA values for COS on freshwater, seawater and substitute seawater

AWS RCA value (Fig. 9.80) is higher for the case of COS on seawater compared to the values corresponding to the same case on freshwater and on substitute seawater. UWS RCA value isn't significantly different among the cases of COS on freshwater, seawater and substitute seawater. In all these cases AWS RCA values aren't significantly different compared to the relevant UWS RCA values.

9.8 Comparisons between straw and trade sorbents adsorbency

In this section, adsorbency of straw (AWS, AcWS, ABS and AcBS) and trade sorbents (oil adsorbent pad, oil adsorbent pom-poms), on pure liquids, was thoroughly compared in order to display the differences on adsorptivity between the straw (wheat and barley) and the trade sorbents. Furthermore, the adsorption capacity of wheat straw (UWS and AWS) in the cases of DOS and COS on: freshwater and seawater was compared with this of the trade sorbents in order to determine the differences.

Comparison among UWS, AWS and trade sorbents adsorbency on pure liquids

Water, diesel oil and crude oil adsorbency values of AWS (Table 9.9) were found comparable to the absorbencies of the most commonly used commercial polypropylene oil adsorbent pad "Scorpion P-200" (Fig. 9.81) and pom-poms oil trap (Fig. 9.82) in the case of pure liquids.

Fig. 9.81 Oil adsorbent pad "Scorpion P-200"

Fig. 9.82 Pom-poms oil trap

Table 9.9 Water, diesel oil and crude oil adsorbency of UWS and AWS (at 200^{o}C for 0 min) vs. the most commonly used commercial adsorbents; the case of pure liquids

		Adsorbency (g/g)			
Oil	Sorbents	Water	Oil	Total	Relative
	Pure liquids				
None	Untreated wheat straw	4.89			
	Pretreated wheat straw	12.67			
	Oil adsorbent pad	0.99			
	Oil adsorbent pom-poms	3.35			
Crude oil	Untreated wheat straw		2.82		
	Pretreated wheat straw		7.28		
	Oil adsorbent pad		12.21		
	Oil adsorbent pom-poms		5.06		
Diesel oil	Untreated wheat straw		2.77		
	Pretreated wheat straw		7.83		
	Oil adsorbent pad		10.26		
	Oil adsorbent pom-poms		3.68		

Comparison among UWS, AcWS and trade sorbents adsorbency on pure liquids

Water, diesel oil and crude oil adsorbency values of AcWS (Table 9.10) were found comparable to the absorbencies of the most commonly used commercial polypropylene oil adsorbent pad and pom-poms in the case of pure liquids.

Table 9.10 Water, diesel oil and crude oil adsorbency of UWS and AcWS (at 160^{o}C for 20 min) vs. the most commonly used commercial adsorbents; the case of pure liquids

		Adsorbency (g/g)			
Oil	Sorbents	Water	Oil	Total	Relative
	Pure liquids				
None	Untreated wheat straw	4.89			
	Pretreated wheat straw	7.44			
	Oil adsorbent pad	0.99			
	Oil adsorbent pom-poms	3.35			
Crude oil	Untreated wheat straw		2.82		
	Pretreated wheat straw		5.38		
	Oil adsorbent pad		12.21		
	Oil adsorbent pom-poms		5.06		
Diesel oil	Untreated wheat straw		2.77		
	Pretreated wheat straw		5.24		
	Oil adsorbent pad		10.26		
	Oil adsorbent pom-poms		3.68		

Comparison among UBS, ABS and trade sorbents adsorbency on pure liquids

Water, diesel oil and crude oil adsorbency values of ABS (Table 9.11) were found comparable to the absorbencies of the most commonly used commercial polypropylene oil adsorbent pad and pom-poms in the case of pure liquids.

Table 9.11 Water, diesel oil and crude oil adsorbency of UBS and ABS (at 180^{o}C for 30 min) vs. the most commonly used commercial adsorbents; the case of pure liquids

		Adsorbency (g/g)			
Oil	Sorbents	Water	Oil	Total	Relative
	Pure liquids				
None	Untreated barley straw	5.12			
	Pretreated barley straw	10.98			
	Oil adsorbent pad	0.99			
	Oil adsorbent pom-poms	3.35			
Crude oil	Untreated barley straw		4.05		
	Pretreated barley straw		8.28		
	Oil adsorbent pad		12.21		
	Oil adsorbent pom-poms		5.06		
Diesel oil	Untreated barley straw		3.38		
	Pretreated barley straw		6.86		
	Oil adsorbent pad		10.26		
	Oil adsorbent pom-poms		3.68		

Comparison among UBS, AcBS and trade sorbents adsorbency on pure liquids

Water, diesel oil and crude oil adsorbency values of AcBS (Table 9.12) were found comparable to the absorbencies of the most commonly used commercial polypropylene oil adsorbent pad and pom-poms in the case of pure liquids.

Table 9.12 Water, diesel oil and crude oil adsorbency of UBS and AcBS (at 160^{o}C for 40 min) vs. the most commonly used commercial adsorbents; the case of pure liquids

		Adsorbency (g/g)			
Oil	Sorbents	Water	Oil	Total	Relative
	Pure liquids				
None	Untreated barley straw	5.12			
	Pretreated barley straw	11.95			
	Oil adsorbent pad	0.99			
	Oil adsorbent pom-poms	3.35			
Crude oil	Untreated barley straw		4.05		
	Pretreated barley straw		8.64		
	Oil adsorbent pad		12.21		
	Oil adsorbent pom-poms		5.06		
Diesel oil	Untreated barley straw		3.38		
	Pretreated barley straw		6.74		
	Oil adsorbent pad		10.26		
	Oil adsorbent pom-poms		3.68		

Comparison among UWS, AWS and trade sorbents adsorbency in the case of oil spills on freshwater/ seawater

Water, diesel and crude oil adsorbencies values of untreated (UWS) and autohydrolyzed wheat straw (AWS) compared with the most commonly used commercial adsorbents (oil adsorbent pad and pom-poms) are given in Tables 9.13 and 9.14, in the cases of oil spills on freshwater and oil spills on seawater, respectively. In the case of diesel oil spill on freshwater and seawater, autohydrolyzed wheat straw (at optimal conditions, i.e., log R_0=5.15 at 200^{o}C for 10 min, not including preheating time) was found to have higher oil adsorbency comparing to the commercial pom-poms. Moreover, in the case of crude oil spill on freshwater, autohydrolyzed wheat straw oil adsorbency was comparable to the commercial oil adsorbent pad and pom-poms. The modified wheat straw has similar sorption capacity comparing to the commercial adsorbents, nevertheless shows high biodegradability and cost-effectiveness.

Table 9.13 Water, diesel and crude oil adsorbency of untreated and autohydrolyzed wheat straw vs. the most commonly used commercial adsorbents in the case of oil spills on freshwater

		Adsorbency (g/g)			
Oil	Sorbents	Water	Oil	Total	Relative
	Oil spill on freshwater				
Crude oil	Oil adsorbent pad	0.81	9.82	10.63	92.4%
	Oil adsorbent pom-poms	0.67	7.77	8.45	92.0%
	Untreated wheat straw	1.29	4.36	5.65	77.1%
	Pretreated wheat straw	2.82	8.36	11.18	74.8%
Diesel oil	Oil adsorbent pad	0.53	9.02	9.55	94.5%
	Oil adsorbent pom-poms	1.41	4.16	5.57	74.7%
	Untreated wheat straw	1.68	3.17	4.86	65.3%
	Pretreated wheat straw	1.18	6.13	7.31	83.9%

Table 9.14 Water, diesel and crude oil adsorbency of untreated and autohydrolyzed wheat straw vs. the most commonly used commercial adsorbents in the case of oil spills on seawater

		Adsorbency (g/g)			
Oil	Sorbents	Water	Oil	Total	Relative
	Oil spill on seawater				
Crude oil	Oil adsorbent pad	0.14	9.51	9.64	98.6%
	Oil adsorbent pom-poms	0.28	7.88	8.16	96.6%
	Untreated wheat straw	0.94	4.08	5.02	81.3%
	Pretreated wheat straw	1.76	6.91	8.67	79.7%
Diesel oil	Oil adsorbent pad	0.13	9.51	9.64	98.6%
	Oil adsorbent pom-poms	0.28	5.25	5.53	94.9%
	Untreated wheat straw	0.88	2.76	3.64	75.7%
	Pretreated wheat straw	2.72	6.65	9.37	70.9%

The comparison of oil adsorbency efficiency of the adsorbents used in this study to the untreated/modified lignocellulosic adsorbents presented in recent literature is shown in Table 9.15, where no previous work with untreated wheat straw appears to have been published. It should be mentioned that there was a great variety of oil types, media and methods used for the estimation of the adsorbency, leading to a wide range of adsorbency values and making a general comparison rather difficult. Nevertheless, we can discriminate three clusters that might be characterized more close to this study, as regards the usage of similar raw material. The first cluster is based on the usage of untreated barley straw with adsorption capacities 7.80-12.20

g/g, i.e., higher than 2.76-4.08 g/g, which are the results for untreated wheat straw used in the present study. The second cluster is based on the usage of modified barley, rice and wheat straw (the last two appearing in only one report each) with adsorption capacities 0.58-28.80 g/g comparable to 6.85-6.91 g/g for modified wheat straw in the present work.

Table 9.15 Comparison of oil adsorbency of the adsorbents used in this study to the untreated/modified lignocellulosic adsorbents presented in the recent literature

Adsorbent	Oil Type	Adsorbency (g/g)	Media	Reference
Banana trunk fiber	Car engine oil	2.06	Oil spill on water	Sathasivam and Haris (2010)
Banana trunk fiber (castor oil treated)	Car engine oil	8.90	Oil spill on water	Sathasivam and Haris (2010)
Banana trunk fiber (oleic acid treated)	Car engine oil	10.78	Oil spill on water	Sathasivam and Haris (2010)
Banana trunk fiber (palm oil treated)	Car engine oil	7.65	Oil spill on water	Sathasivam and Haris (2010)
Banana trunk fiber (stearic acid treated)	Car engine oil	9.58	Oil spill on water	Sathasivam and Haris (2010)
Barley straw	Crude oil	12.20	Oil spill on substitute seawater	Husseien et al. (2009)
Barley straw	Gas oil	7.80	Oil spill on substitute seawater	Husseien et al. (2009)
Barley straw (heated)	Crude oil	9.20	Pure oil	Husseien et al. (2008)
Barley straw (heated)	Gas oil	7.60	Pure oil	Husseien et al. (2008)
Barley straw (NaOH treated)	Mineral oil	0.58	Oil spill on water	Ibrahim et al. (2009)
Barley straw (NaOH treated)	Canola oil	0.58	Oil spill on water	Ibrahim et al. (2010)
Fir fibers (carbonized)	Heavy oil	80.00	Pure oil	Inagaki et al. (2002)
Garlic peels	Crude oil	0.39	Oil spill on saltwater	Sayed and Zayed (2006)
Groundnut husks	Crude oil	1.11	Oil spill on water	Nwokoma and Avene (2010)
Oil adsorbent pad	Diesel	9.51	Oil spill on seawater	Measured in this study
Oil adsorbent pad	Crude oil	9.51	Oil spill on seawater	Measured in this study
Oil adsorbent pom-poms	Diesel	5.25	Oil spill on seawater	Measured in this study
Oil adsorbent pom-poms	Crude oil	7.88	Oil spill on seawater	Measured in this study
Onion peels	Crude oil	0.46	Oil spill on saltwater	Sayed and Zayed (2006)
Pith bagasse (carbonized)	Crude oil	25.50	Pure oil	Hussein et al. (2008)
Pith bagasse (carbonized)	Gas oil	23.86	Pure oil	Hussein et al. (2008)

Rice husk (carbonized)	Heavy oil	6.70	Pure oil	Kumagai et al. (2007)
Rice husks (carbonized)	Gasoline oil	3.70	Pure oil	Angelova et al. (2011)
Rice husks (carbonized)	Diesel	5.50	Pure oil	Angelova et al. (2011)
Rice husks (carbonized)	Motor oil	7.50	Pure oil	Angelova et al. (2011)
Rice husks (carbonized)	Light crude oil	6.00	Pure oil	Angelova et al. (2011)
Rice husks (carbonized)	Heavy crude oil	9.20	Pure oil	Angelova et al. (2011)
Rice straw (acetylated)	Machine oil	24.00	Oil spill on water	Sun et al. (2002)
Sawdust (oleic acid grafted)	Crude oil	6.40	Oil spill on seawater	Banerjee et al. (2006a)
Sugarcane bagasse (acetylated)	Machine oil	20.20	Oil spill on water	Sun et al. (2004b)
Walnut shell	Light oil	0.56	Oil spill on water	Srinivasan and Viraraghavan (2008)
Walnut shell	Vegetable oil	0.58	Oil spill on water	Srinivasan and Viraraghavan (2008)
Walnut shell	Cutting oil	0.74	Oil spill on water	Srinivasan and Viraraghavan (2008)
Wheat straw (acetylated)	Machine oil	28.80	Oil spill on water	Sun et al. (2004a)
Wheat straw (autohydrolyzed)	Diesel	6.65	Oil spill on seawater	This study
Wheat straw (autohydrolyzed)	Crude oil	6.91	Oil spill on seawater	This study
Wheat straw untreated	Diesel oil	2.76	Oil spill on seawater	This study
Wheat straw untreated	Crude oil	4.08	Oil spill on seawater	This study

The third cluster is based on the usage of modified rice husk with adsorption capacities 3.70-9.20 g/g also comparable to the same range 6.85-6.91 g/g for modified wheat straw investigated herein. According to Safarik et al. (2005) adsorbent can also be magnetically modified after contact with water-based magnetic fluid in a simple and inexpensive way. Magnetic behavior of the adsorbent enables its rapid and efficient removal after its use in open sea. Moreover, straw can be applied enclosed or pressed to a mat-form (Suni et al., 2004).

CHAPTER 10
FACTORS EFFECTING WHEAT STRAW ADSORPTIVITY

10.1 Effect of harvesting year on wheat straw adsorptivity

In sub-chapter 9.3, the adsorption capacity of untreated and auto-hydrolyzed (at 200^{o}C, for 10 min isothermal reaction time following a non-isothermal preheating period) wheat straw harvested at 2009 (wheat straw I) in the cases of pure liquids (water, diesel oil and crude oil), DOS and COS on fresh and seawater was determined. In the present sub-chapter the adsorption capacity of wheat straw harvested at 2012 (wheat straw II) for the same cases was examined and compared to the adsorption capacity of the wheat straw I. Statistical analysis, taking into account the experimental error resulting from the repeatability measurements, was done.

10.1.1 Pure liquids

Untreated and auto-hydrolyzed wheat straw II (UWS-II and AWS-II, respectively), were examined as regards their adsorption capacities in the case of pure water, diesel oil and crude oil.

Table 10.1(a) Water, diesel oil and crude oil adsorbency of UWS II and AWS II vs. UWS I and AWS I; the case of pure liquids

		Adsorbency (g/g)			
Oil	Sorbents	Water	Oil	Total	Relative
	Pure				
None	UWS-II	4.29			
	UWS-I	4.89			
	AWS-II	7.72			
	AWS-I	11.93			
Crude oil	UWS-II		4.70		
	UWS-I		2.82		
	AWS-II		9.05		
	AWS-I		5.27		
Diesel oil	UWS-II		2.51		
	UWS-I		2.77		
	AWS-II		6.05		
	AWS-I		7.15		

The results were compared to those of the wheat straw I to find out the influence of the different harvesting year on the adsorption capacity of the straw.

More specifically (Table 10.1a), water adsorbency values of the UWS-II and AWS-II slightly decreased and decreased 21.4%, comparing to those of the wheat straw I, respectively. Crude oil adsorbency values of the UWS-II and AWS-II increased 25.0% and 26.4%, comparing to those of the wheat straw I, respectively. There was no significant difference as regards diesel oil adsorbency values of the AWS-II while for AWS-II was slightly decreased, comparing to those of the wheat straw I, respectively.

10.1.2 Oil spill on freshwater

The UWS-II and AWS-II were examined as regards their adsorption capacities in the case of DOS and COS on freshwater. The results were compared to those of the wheat straw I to find out the influence of the different harvesting year on the adsorption capacity of the straw.

More specifically (Table 10.1b), there was no significant difference as regards water adsorbency values, in COS, for the UWS-II while for AWS-II was decreased 43.1%, comparing to those of the wheat straw I, respectively. Water adsorbency values, in DOS, for the UWS-II decreased 33.3% while for AWS-II presented no significant difference, comparing to those of the wheat straw I, respectively. Consequently, as regards oil adsorbency values, in COS and DOS, of the wheat straw II compared to those of the wheat straw I, for both untreated and pretreated wheat straw, weren't significantly different.

Table 10.1(b) Water, diesel oil and crude oil adsorbency of UWS-II and AWS-II vs. UWS-I and AWS-I; the case of oil spills on freshwater

		Adsorbency (g/g)			
Oil	Sorbents	Water	Oil	Total	Relative
	Oil spill on freshwater				
Crude oil	UWS-II	1.09	4.90	6.00	81.8%
	UWS-I	1.29	4.36	5.65	77.1%
	AWS-II	1.12	9.99	11.10	90.0%
	AWS-I	2.82	8.36	11.18	74.8%
Diesel oil	UWS-II	0.84	3.58	4.42	81.0%
	UWS-I	1.68	3.17	4.86	65.3%
	AWS-II	1.73	6.89	8.62	79.9%
	AWS-I	1.18	6.13	7.31	83.9%

Accordingly, as regards total adsorbency and RCA values, in COS, of the wheat straw II compared to those of the wheat straw I, for both untreated and pretreated wheat straw, weren't significantly different. Total adsorbency values in DOS of the UWS-II and AWS-II slightly decreased and slightly increased, comparing to those of the wheat straw I, respectively. Finally, RDA values, in DOS, of the UWS-II increased 10.7% while for AWS-II presented no significant difference, comparing to those of the wheat straw I, respectively.

10.1.3 Oil spill on seawater

The UWS-II and AWS-II were examined as regards their adsorption capacities in the case of DOS and COS on seawater. The results were compared to those of the wheat straw I to find out the influence of the different harvesting year on the adsorption capacity of the straw. More specifically (Table 10.1c), there was no significant difference in water adsorbency values in COS of the UWS-II while for AWS-II was decreased 44.3%, comparing to those of the wheat straw I, respectively. Consequently, as regards water adsorbency values in DOS of the wheat straw II compared to those of the wheat straw I, for both untreated and pretreated wheat straw, weren't significantly different. There was no significant difference in oil adsorbency values, in COS, of the UWS-II while for AWS-II was increased 16.5%, comparing to those of the wheat straw I, respectively.

Table 10.1(c) Water, diesel oil and crude oil adsorbency of untreated and autohydrolyzed wheat straw II vs. wheat straw I in the case of oil spills on seawater

		Adsorbency (g/g)			
Oil	Sorbents	Water	Oil	Total	Relative
	Oil spill on seawater				
Crude oil	UWS-II	1.05	4.71	5.76	81.8%
	UWS-I	0.94	4.08	5.02	81.3%
	AWS-II	0.68	9.64	10.33	93.4%
	AWS-I	1.76	6.91	8.67	79.7%
Diesel oil	UWS-II	1.10	3.39	4.49	75.4%
	UWS-I	0.88	2.76	3.64	75.7%
	AWS-II	1.45	6.46	7.91	81.6%
	AWS-I	2.72	6.65	9.37	70.9%

Oil adsorbency values, in DOS, of the UWS-II increased 10.2% while for AWS-II presented no significant difference, comparing to those of the wheat straw I, respectively. Accordingly, as regards total adsorbency, RCA and RDA values, in COS and DOS, of the wheat straw II compared to those of the wheat straw I, for both untreated and pretreated wheat straw, weren't significantly different.

10.2 Effect of net packaging on wheat straw adsorptivity

As it was mentioned in sub-chapter 9.1, two methods are simple and inexpensive in order to put out the used adsorbent from the open sea in real oil spill conditions: magnetically modification of the adsorbent (wheat straw) after its contact with water-based magnetic fluid (Safarik et al., 2005). Moreover, straw can be applied enclosed or pressed to a mat-form (Suni et al., 2004). In this subchapter, the influence of packing the wheat straw II (untreated and autohydrolyzed) with a polypropylene net (Fig. 10.1), on its adsorption capacity was examined, in the cases of pure liquids (water, diesel oil and crude oil), DOS and COS on fresh and seawater. Statistical analysis, taking into account the experimental error resulting from the repeatability measurements, was done.

10.2.1 Pure liquids

Untreated and autohydrolyzed packed wheat straw II, were examined as regards their adsorption capacities in the case of pure water, diesel oil and crude oil (Fig. 10.2). The results were compared to those of the unpacked wheat straw II to find out the influence of packing the straw on its adsorption capacity. More specifically (Table 10.2a), water adsorbency values of the packed UWS-II and AWS-II, slightly decreased and increased 15.2%, comparing to those of the unpacked material, respectively.

Fig. 10.1 Packed UWS-II (left) and packed AWS-II (right)

Table 10.2(a) Water, diesel oil and crude oil adsorbency of UWS-II and AWS-II vs. packed UWS-II and AWS-II; the case of pure liquids

		Adsorbency (g/g)			
Oil	Sorbents	Water	Oil	Total	Relative
	Pure				
None	UWS-II	4.29			
	Packed UWS-II	3.99			
	AWS-II	7.72			
	Packed AWS-II	8.89			
Crude oil	UWS-II		4.70		
	Packed UWS-II		4.11		
	AWS-II		9.05		
	Packed AWS-II		6.86		
Diesel oil	UWS-II		2.51		
	Packed UWS-II		2.23		
	AWS-II		6.05		
	Packed AWS-II		5.83		

Crude oil adsorbency values of the packed UWS-II and AWS-II, decreased 12.6% and 24.2%, comparing to those of the same unpacked straw, respectively. Diesel oil adsorbency of the packed UWS-II, decreased 11.2% comparing to that of the same unpacked straw, while in the case of AWS-II there was no significant difference.

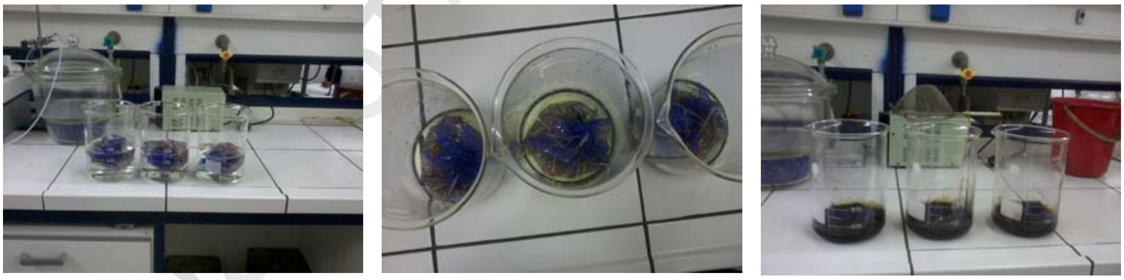


Fig. 10.2 Packed AWS-II in the case of pure liquids experiments; water (left), diesel (middle) and crude oil (right)

10.2.2 Oil spill on freshwater

The packed UWS-II and AWS-II, were examined as regards their adsorption capacities in the case of DOS and COS on freshwater. The results were compared to those of the unpacked wheat straw II to find out the influence of packing the straw with a net on its adsorption capacity.

Moreover (Table 10.2b), water adsorbency values in COS of the packed wheat straw II, decreased 76.1% and 54.5%, comparing to those of the same unpacked straw, for both untreated and pretreated wheat straw, respectively. There was no significant difference in water adsorbency values in DOS of the packed UWS-II while for packed AWS-II was decreased 63.0%, comparing to those of the same unpacked straw, respectively.

Table 10.2(b) Water, diesel oil and crude oil adsorbency of UWS-II and AWS-II vs. packed UWS-II and AWS-II; the cases of oil spills on freshwater

		Adsorbency (g/g)			
Oil	Sorbents	Water	Oil	Total	Relative
	Oil spill on freshwater				
Crude oil	UWS-II	1.09	4.90	6.00	81.8%
	Packed UWS-II	0.26	4.09	4.35	94.0%
	AWS-II	1.12	9.99	11.10	90.0%
	Packed AWS-II	0.51	7.91	8.42	93.9%
Diesel oil	UWS-II	0.84	3.58	4.42	81.0%
	Packed UWS-II	0.78	3.03	3.81	79.4%
	AWS-II	1.73	6.89	8.62	79.9%
	Packed AWS-II	0.64	6.61	7.25	91.2%

Consequently, as regards oil adsorbency values, in COS and DOS, of the packed wheat straw II compared to those of the same unpacked straw, for both untreated and pretreated wheat straw weren’t significantly different. Accordingly, as regards total adsorbency and RCA values, in COS, of the packed wheat straw II compared to those of the same unpacked straw, for both untreated and pretreated wheat straw weren’t significantly different.

Total adsorbency values in DOS of the packed wheat straw II, decreased 13.8% and 15.9%, comparing to those of the same unpacked straw, for both untreated and pretreated wheat straw, respectively. Finally, there was no significant difference in RDA values, in DOS, of the packed UWS-II while for packed AWS-II was increased 14.1%, comparing to those of the same unpacked straw, respectively.

10.2.3 Oil spill on seawater

The packed UWS-II and AWS-II, were examined as regards their adsorption capacities in the case of DOS and COS on seawater. The results were compared to those of the unpacked wheat straw II to find out the influence of packing the straw with a net on its adsorption capacity.

Moreover (Table 10.2c), water adsorbency values in COS of the packed wheat straw II, decreased 48.6% and 42.6%, comparing to those of the same unpacked straw, for both untreated and pretreated wheat straw, respectively. There was no significant difference in water adsorbency values in DOS of the packed UWS-II while for packed AWS-II was decreased 73.8%, comparing to those of the same unpacked straw, respectively.

Table 10.2(c) Water, diesel oil and crude oil adsorbency of UWS-II and AWS-II vs. packed UWS-II and AWS-II; the cases of oil spills on seawater

		Adsorbency (g/g)			
Oil	Sorbents	Water	Oil	Total	Relative
	Oil spill on seawater				
Crude oil	UWS-II	1.05	4.71	5.76	81.8%
	Packed UWS-II	0.54	4.27	4.81	88.8%
	AWS-II	0.68	9.64	10.33	93.4%
	Packed AWS-II	0.39	7.69	8.08	95.2%
Diesel oil	UWS-II	1.10	3.39	4.49	75.4%
	Packed UWS-II	1.15	2.84	4.00	71.1%
	AWS-II	1.45	6.46	7.91	81.6%
	Packed AWS-II	0.38	5.96	6.34	94.0%

There was no significant difference in oil adsorbency values, in COS, of the packed UWS-II while for packed AWS-II was decreased 20.2%, comparing to those of the same unpacked straw, respectively. Oil adsorbency values, in DOS of the packed wheat straw II, decreased 16.2% and slightly decreased, comparing to those of the same unpacked straw, for both untreated and pretreated wheat straw, respectively. There was no significant difference in total adsorbency values in COS of the packed UWS-II while for packed AWS-II was decreased 21.8%, comparing to those of the same unpacked straw, respectively.

Consequently, as regards total adsorbency and RDA values, in DOS of the packed wheat straw II compared to those of the same unpacked straw, for both untreated and pretreated wheat straw weren't significantly different. Finally, as regards RCA values, in COS of the packed wheat straw II compared to those of the same unpacked straw, for both untreated and pretreated wheat straw weren't significantly different.

10.3 Effect of chemical dispersant usage on wheat straw adsorptivity

In sub-chapter 9.3, the adsorption capacity of wheat straw (UWS and AWS) in the cases of DOS and COS on fresh and seawater, was determined. In this sub-chapter the adsorption capacity of UWS and AWS (at 160°C, 180°C, 200°C and 240°C, for 0 and 50 min reaction time), with the use of chemical dispersant (UOCD) for the same conditions was examined and compared to the adsorption capacity of the wheat straw, without the UOCD, (Konstantinou and Sidiras, 2014). Then statistical analysis, taking into account the experimental error resulting from the repeatability measurements, was done. The same experimental procedure described in sub-chapter 7.4 was followed adding 50 ml of chemical dispersant diluted 1:10 in water.

10.3.1 Oil spill on fresh water

UWS and AWS with the use of chemical dispersant (UOCD) were examined as regards their adsorption capacities in the case of DOS and COS on freshwater. The results were compared to those of the wheat straw, without the UOCD, to find out the influence of the chemical dispersant usage on the adsorption capacity of the straw. The experimental results of the adsorbencies values for the UWS and the AWS are shown in the following Tables and Figures.

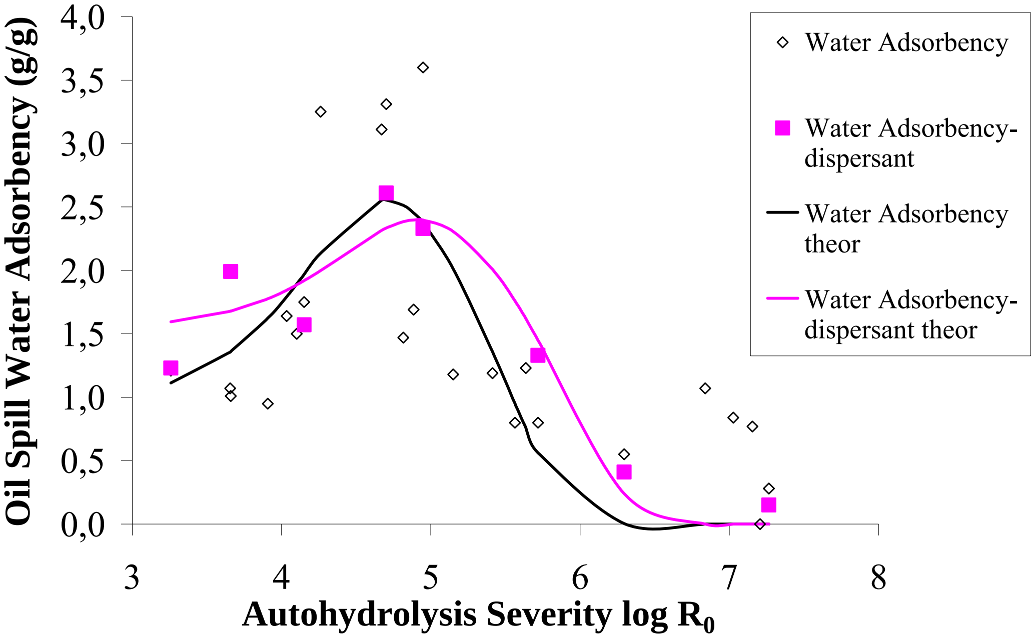


Fig. 10.3 UWS and AWS water adsorbency values vs. Severity Factor R_0 with and without the UOCD; the case of DOS on freshwater

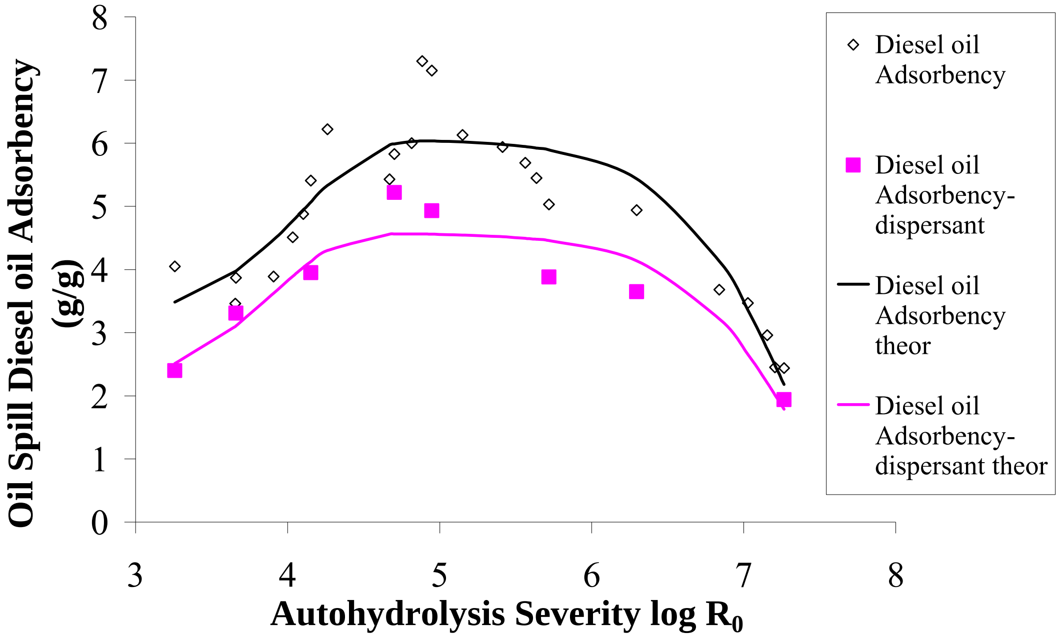


Fig. 10.4 UWS and AWS diesel oil adsorbency values vs. Severity Factor R_0 with and without the UOCD; the case of DOS on freshwater

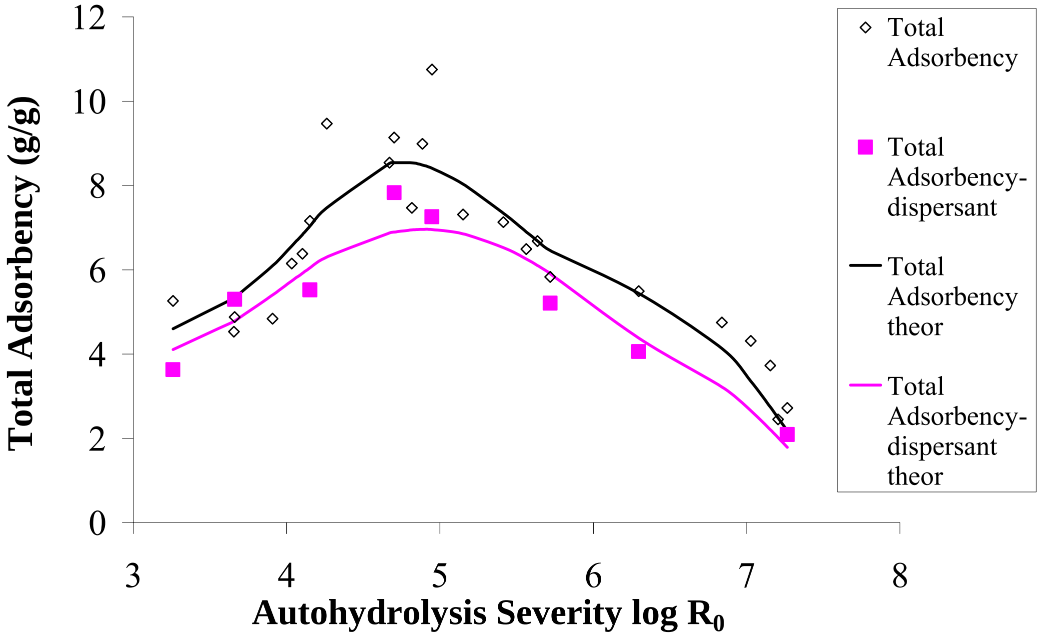


Fig. 10.5 UWS and AWS total adsorbency values vs. Severity Factor R_0 with and without the UOCD; the case of DOS on freshwater

Table 10.3 UWS and AWS adsorbencies values vs. Severity Factor R_0 with and without the UOCD; the case of DOS on freshwater

T (°C)	t (min)	R_0	log R_0	SRY (%)	Water Adsorbency	Water Adsorbency with dispersant	Diesel oil Adsorbency	Diesel oil Adsorbency with dispersant	Total Adsorbency	Total Adsorbency with dispersant	RDA (%)	RDA (%) with dispersant
		$0.00\ 10^{0}$		100.0	1.68	1.78	3.17	2.00	4.85	3.78	65.4	52.9
160	0	$1.81\ 10^{3}$	3.26	90.0	1.21	1.23	4.05	2.40	5.26	3.63	77.0	66.1
160	10	$4.52\ 10^{3}$	3.66	88.2	1.07		3.46		4.53		76.4	
180	0	$4.57\ 10^{3}$	3.66	72.9	1.01	1.99	3.87	3.31	4.88	5.30	79.3	62.5
160	20	$8.09\ 10^{3}$	3.91	86.7	0.95		3.89		4.84		80.4	
160	30	$1.08\ 10^{4}$	4.03	84.6	1.64		4.51		6.15		73.3	
160	40	$1.26\ 10^{4}$	4.10	82.5	1.50		4.88		6.38		76.5	
160	50	$1.42\ 10^{4}$	4.15	80.0	1.75	1.57	5.41	3.95	7.16	5.52	75.6	71.6
180	10	$1.83\ 10^{4}$	4.26	63.7	3.25		6.22		9.47		65.7	
180	20	$4.68\ 10^{4}$	4.67	60.2	3.11		5.43		8.54		63.6	
200	0	$5.03\ 10^{4}$	4.70	53.0	3.31	2.61	5.83	5.22	9.14	7.83	63.8	66.7
180	30	$6.55\ 10^{4}$	4.82	56.7	1.47		6.00		7.47		80.3	
180	40	$7.67\ 10^{4}$	4.88	52.4	1.69		7.30		8.99		81.2	
180	50	$8.87\ 10^{4}$	4.95	51.1	3.60	2.33	7.15	4.93	10.75	7.26	66.5	67.9
200	10	$1.41\ 10^{5}$	5.15	51.9	1.18		6.13		7.31		83.9	
200	20	$2.59\ 10^{5}$	5.41	51.8	1.19		5.94		7.13		83.3	
200	30	$3.66\ 10^{5}$	5.56	50.9	0.80		5.69		6.49		87.7	
200	40	$4.33\ 10^{5}$	5.64	47.0	1.23		5.45		6.68		81.6	
200	50	$5.23\ 10^{5}$	5.72	42.5	0.80	1.33	5.03	3.88	5.83	5.21	86.3	74.5
240	0	$1.98\ 10^{6}$	6.30	45.5	0.55	0.41	4.94	3.65	5.49	4.06	90.0	89.9
240	10	$6.90\ 10^{6}$	6.84	40.2	1.07		3.68		4.75		77.5	
240	20	$1.06\ 10^{7}$	7.03	39.1	0.84		3.47		4.31		80.5	
240	30	$1.43\ 10^{7}$	7.15	37.3	0.77		2.96		3.73		79.4	
240	40	$1.61\ 10^{7}$	7.21	36.2	0.00		2.45		2.45		100.0	
240	50	$1.84\ 10^{7}$	7.27	33.9	0.28	0.15	2.44	1.94	2.72	2.09	89.7	92.8

More specifically, there was no significant difference as regards water adsorbency values in DOS on freshwater with the UOCD (Fig. 10.3) comparing to those of the wheat straw without the UOCD. Diesel oil adsorbency, total adsorbency and RDA values with the UOCD (Figs 10.4, 10.5 and 10.6) decreased comparing to those of the wheat straw without the UOCD.

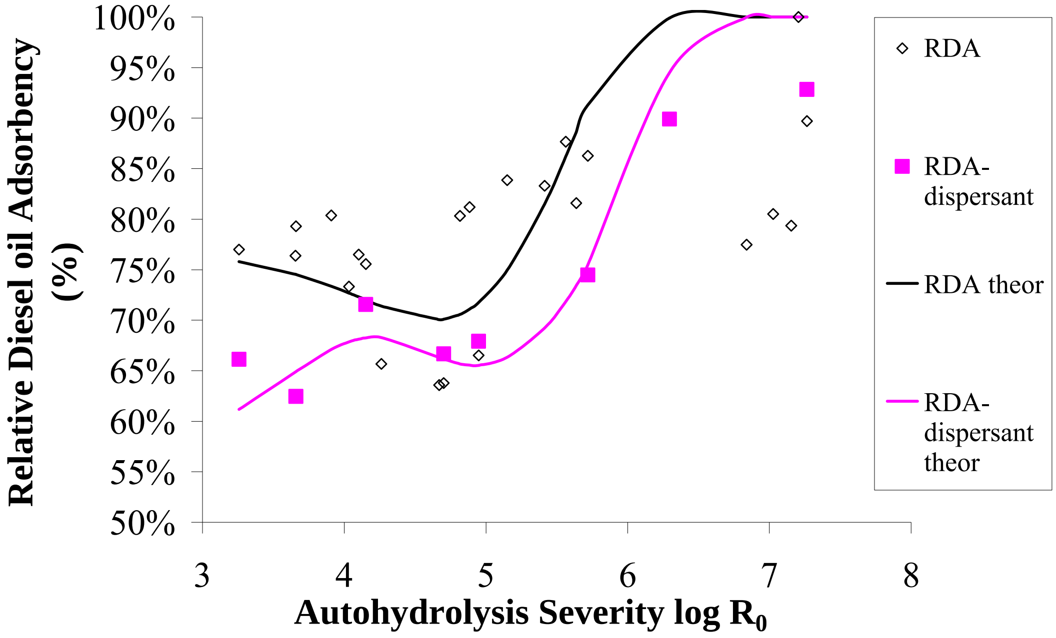
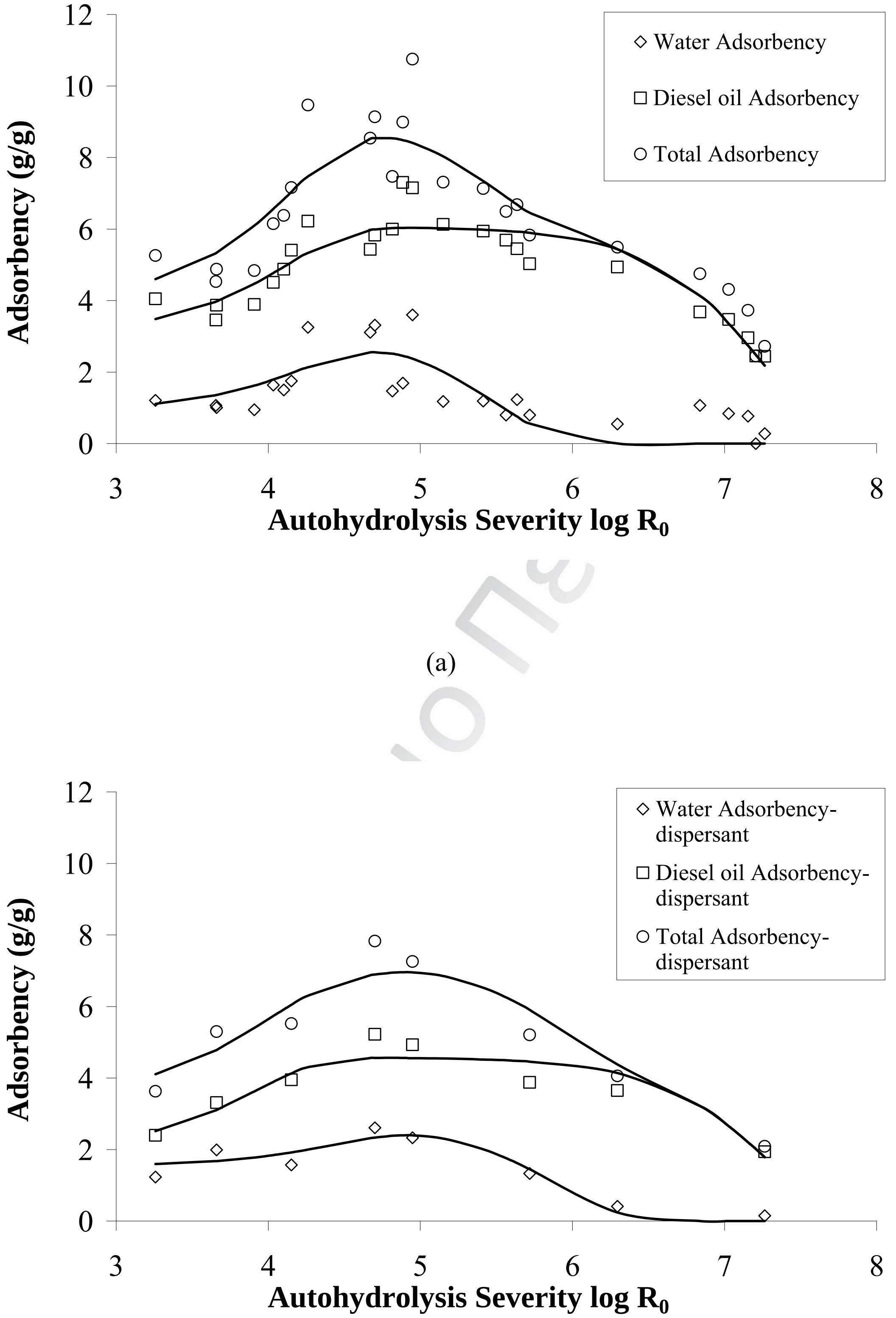


Fig. 10.6 UWS and AWS RDA values vs. Severity Factor R_0 with and without the UOCD; the case of DOS on freshwater

Table 10.4 Simulation model parameters of UWS and AWS adsorbencies values with and without the UOCD; the case of DOS on freshwater

Parameters	Water Adsorbency	Diesel oil Adsorbency	Water Adsorbency with dispersant	Diesel oil Adsorbency with dispersant
$a_1 = A'\infty - A_0$	46.3	8384.8	65.4	11019.2
b_1	$3.34\ 10^{-6}$	$5.56\ 10^{-8}$	$1.24\ 10^{-6}$	$5.11\ 10^{-8}$
$a_2 = A_0$	0.928	3.098	1.534	1.996
b_2	$5.13\ 10^{-5}$	$7.69\ 10^{-5}$	$3.05\ 10^{-5}$	$1.23\ 10^{-4}$
sum	10.592	6.706	0.557	1.253
n'	25	25	9	9
p'	4	4	4	4
SEE	0.7102	0.5651	0.3340	0.5006



(a)

(b)

Fig. 10.7 UWS and AWS adsorbencies values vs. Severity Factor R_0 (a) without and (b) with the UOCD; the case of DOS on freshwater

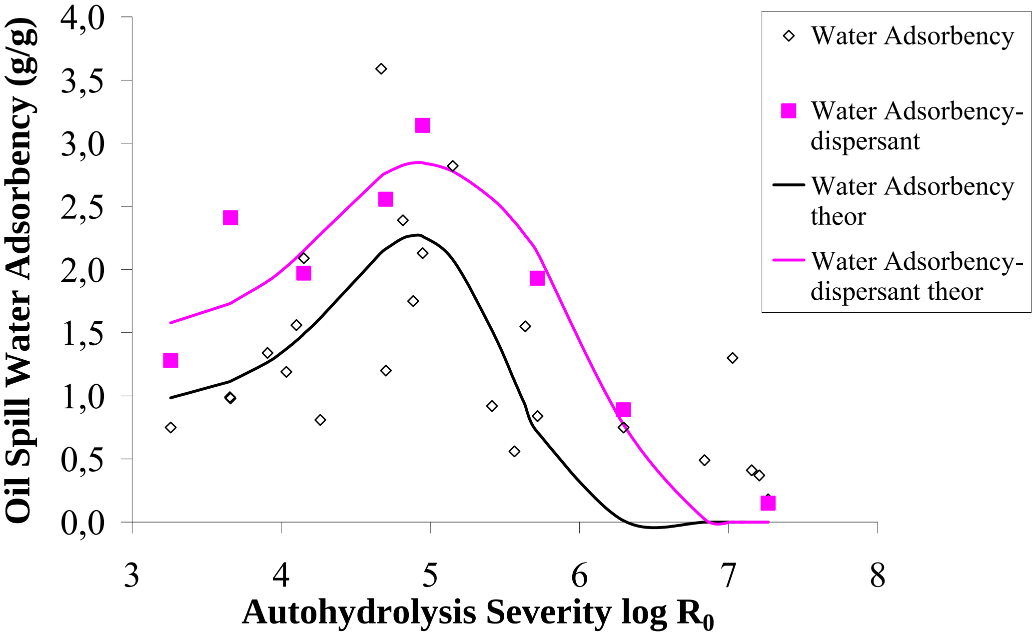


Fig. 10.8 UWS and AWS water adsorbency values vs. Severity Factor R_0 with and without the UOCD; the case of COS on freshwater

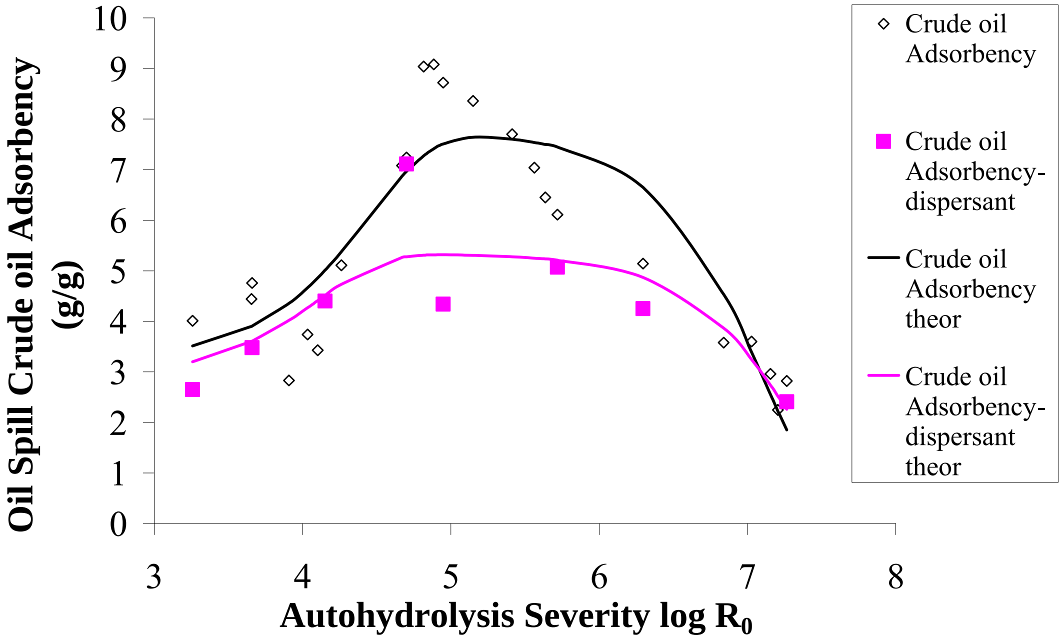


Fig. 10.9 UWS and AWS crude oil adsorbency values vs. Severity Factor R_0 with and without the UOCD; the case of COS on freshwater

Table 10.5 UWS and AWS adsorbencies values vs. Severity Factor R_0 with and without the UOCD; the case of COS on freshwater

T (°C)	t (min)	R_0	log R_0	SRY (%)	Water Adsorbency	Water Adsorbency with dispersant	Crude oil Adsorbency	Crude oil Adsorbency with dispersant	Total Adsorbency	Total Adsorbency with dispersant	RCA (%)	RCA (%) with dispersant
		$0.00\ 10^0$		100.0	1.29	1.30	4.36	3.45	5.65	4.75	77.2	72.6
160	0	$1.81\ 10^3$	3.26	90.0	0.75	1.28	4.01	2.65	4.76	3.93	84.2	67.4
160	10	$4.52\ 10^3$	3.66	88.2	0.99		4.44		5.43		81.8	
180	0	$4.57\ 10^3$	3.66	72.9	0.98	2.41	4.76	3.48	5.74	5.89	82.9	59.1
160	20	$8.09\ 10^3$	3.91	86.7	1.34		2.83		4.17		67.9	
160	30	$1.08\ 10^4$	4.03	84.6	1.19		3.74		4.93		75.9	
160	40	$1.26\ 10^4$	4.10	82.5	1.56		3.43		4.99		68.7	
160	50	$1.42\ 10^4$	4.15	80.0	2.09	1.97	4.39	4.40	6.48	6.37	67.7	69.1
180	10	$1.83\ 10^4$	4.26	63.7	0.81		5.11		5.92		86.3	
180	20	$4.68\ 10^4$	4.67	60.2	3.59		7.08		10.67		66.4	
200	0	$5.03\ 10^4$	4.70	53.0	1.20	2.55	7.24	7.11	8.44	9.67	85.8	73.6
180	30	$6.55\ 10^4$	4.82	56.7	2.39		9.04		11.43		79.1	
180	40	$7.67\ 10^4$	4.88	52.4	1.75		9.08		10.83		83.8	
180	50	$8.87\ 10^4$	4.95	51.1	2.13	3.14	8.72	4.34	10.85	7.48	80.4	58.0
200	10	$1.41\ 10^5$	5.15	51.9	2.82		8.36		11.18		74.8	
200	20	$2.59\ 10^5$	5.41	51.8	0.92		7.70		8.62		89.3	
200	30	$3.66\ 10^5$	5.56	50.9	0.56		7.04		7.60		92.6	
200	40	$4.33\ 10^5$	5.64	47.0	1.55		6.45		8.00		80.6	
200	50	$5.23\ 10^5$	5.72	42.5	0.84	1.93	6.11	5.07	6.95	7.00	87.9	72.4
240	0	$1.98\ 10^6$	6.30	45.5	0.75	0.89	5.14	4.25	5.89	5.14	87.3	82.7
240	10	$6.90\ 10^6$	6.84	40.2	0.49		3.58		4.07		88.0	
240	20	$1.06\ 10^7$	7.03	39.1	1.30		3.60		4.90		73.5	
240	30	$1.43\ 10^7$	7.15	37.3	0.41		2.96		3.37		87.8	
240	40	$1.61\ 10^7$	7.21	36.2	0.37		2.25		2.62		85.9	
240	50	$1.84\ 10^7$	7.27	33.9	0.18	0.15	2.82	2.41	3.00	2.56	94.0	94.1

Water, diesel oil and total adsorbency and RDA values of UWS and AWS in the cases of DOS on freshwater with and without the UOCD are given in Table 10.3. The same conclusions derived from Fig. 10.7, where water adsorbency, diesel oil adsorbency and total adsorbency curves are shown in the case without the UOCD (Fig. 10.7a) and in the case with the UOCD (Fig. 10.7b). Consequently, as regards water adsorbency values in COS on freshwater with the UOCD (Fig. 10.8) increased comparing to those of the wheat straw without the UOCD.

The empirical constants' values a_1, b_1, a_2, b_2 of UWS and AWS adsorbencies values with and without the UOCD in the case of DOS on freshwater were estimated using NLRA. These values and the SEE values are presented in Table 10.4.

Crude oil adsorbency and RCA values with the UOCD (Figs 10.9 and 10.11) decreased comparing to those of the wheat straw without the UOCD, while at the maximum adsorption points, total adsorbency values with the UOCD (Fig. 10.10) slightly increased comparing to those of the wheat straw without the UOCD. Water, crude oil and total adsorbency and RCA values of UWS and AWS in the cases of COS on freshwater with and without the UOCD are given in Table 10.5.

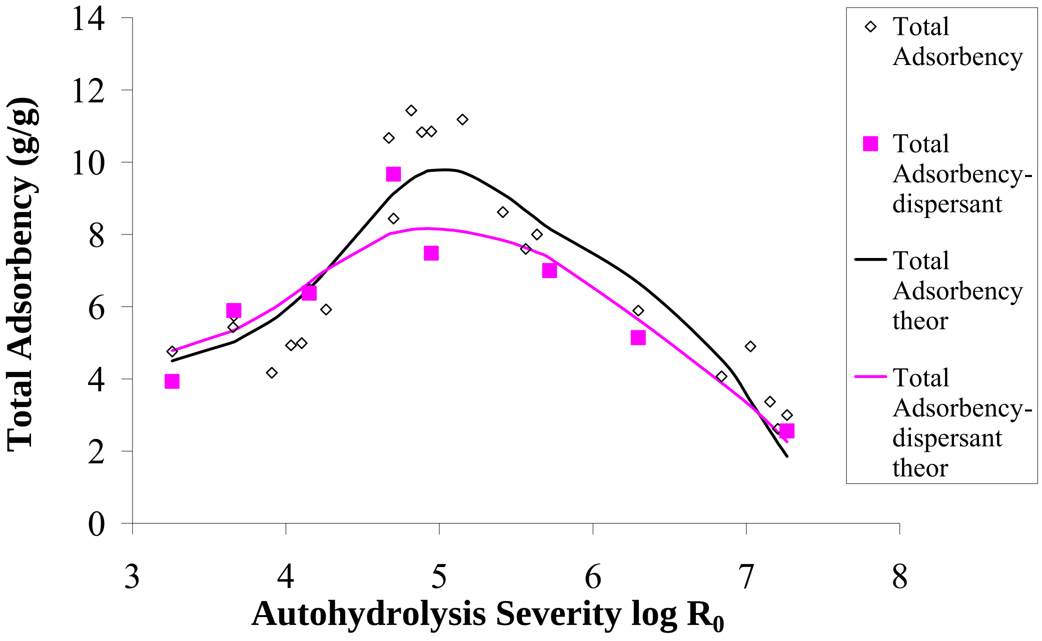


Fig. 10.10 UWS and AWS total adsorbency values vs. Severity Factor R_0 with and without the UOCD; the case of COS on freshwater

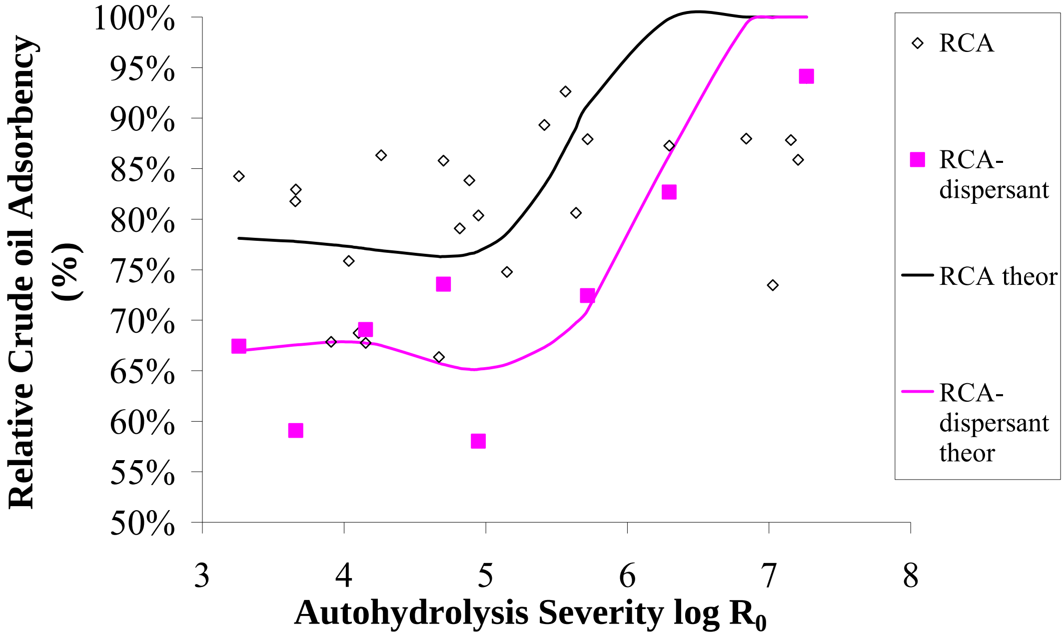
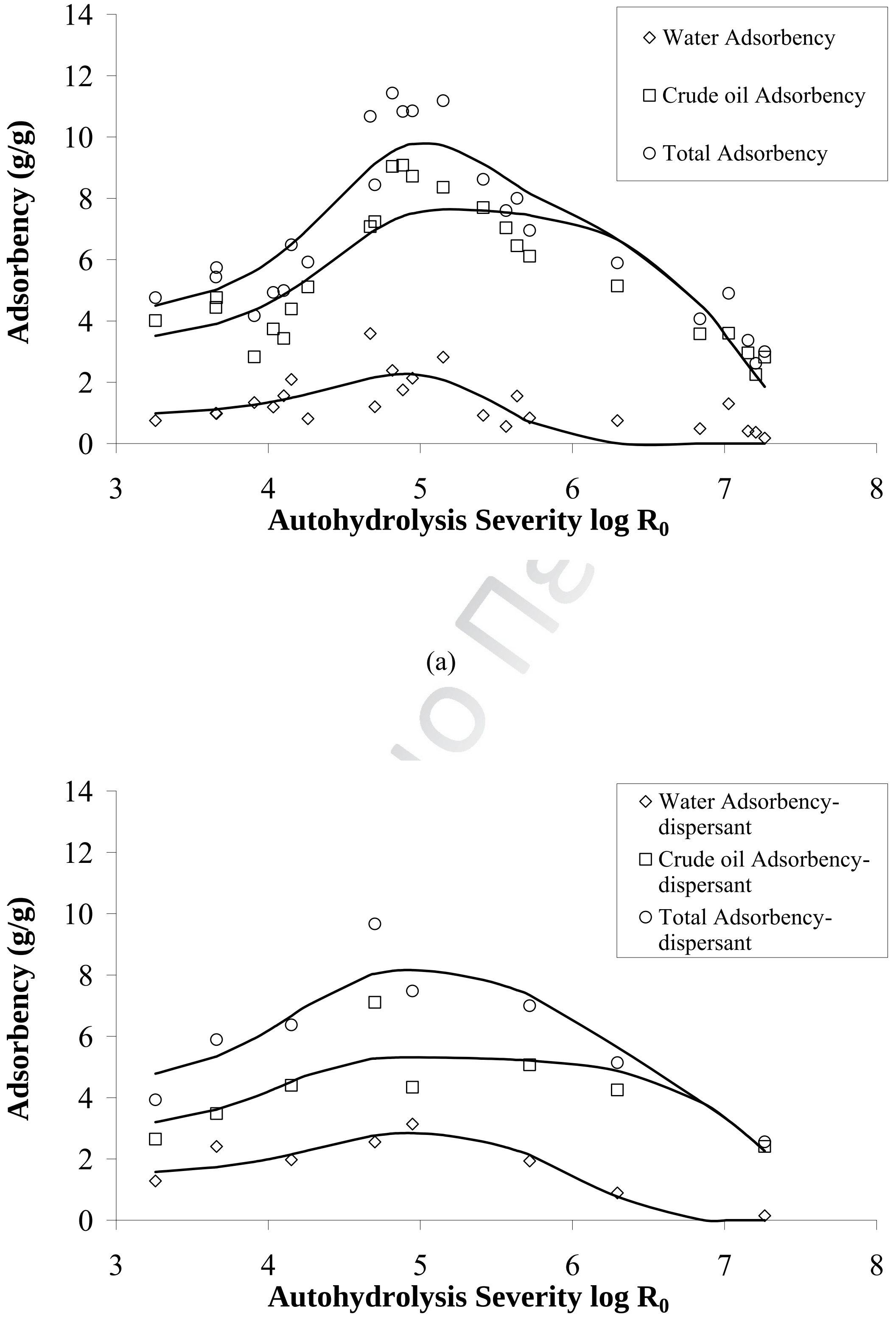


Fig. 10.11 UWS and AWS RCA values vs. Severity Factor R_0 with and without the UOCD; the case of COS on freshwater

Table 10.6 Simulation model parameters of UWS and AWS adsorbencies values with and without the UOCD; the case of COS on freshwater

Parameters	Water Adsorbency	Crude oil Adsorbency	Water Adsorbency with dispersant	Crude oil Adsorbency with dispersant
$a_1 = A'^{\infty} - A_0$	26.4	3530.6	467.9	8799.8
b_1	$2.87\ 10^{-6}$	$7.77\ 10^{-8}$	$6.15\ 10^{-7}$	$9.08\ 10^{-8}$
$a_2 = A_0$	0.892	3.232	1.031	3.344
b_2	$2.66\ 10^{-5}$	$3.55\ 10^{-5}$	$1.11\ 10^{-4}$	$1.50\ 10^{-4}$
sum	9.110	23.719	0.666	7.337
n'	25	25	9	9
p'	4	4	4	4
SEE	0.6586	1.0627	0.4035	1.0388

The same conclusions derived from Fig. 10.12, where water adsorbency, crude oil adsorbency and total adsorbency curves are shown in the case without the UOCD (Fig. 10.12a) and in the case with the UOCD (Fig. 10.12b). The empirical constants' values a_1, b_1, a_2, b_2 of UWS and AWS adsorbencies values with and without the UOCD in the case of COS on freshwater were estimated using NLRA. These values and the SEE values are presented in Table 10.6.



(a)

(b)

Fig. 10.12 UWS and AWS adsorbencies values vs. Severity Factor R_0 (a) without and (b) with the UOCD; the case of COS on freshwater

10.3.2 Oil spill on seawater

UWS and AWS with the use of chemical dispersant (UOCD) were examined as regards their adsorption capacities in the case of DOS and COS on seawater. The results were compared to those of the wheat straw, without the UOCD, to find out the influence of the chemical dispersant usage on the adsorption capacity of the straw.

The experimental results of the adsorbencies values for the UWS and the AWS are shown in the following Tables and Figures. More specifically, there was no significant difference as regards water adsorbency values in DOS on seawater with the UOCD (Fig. 10.13) comparing to those of the wheat straw without the UOCD.

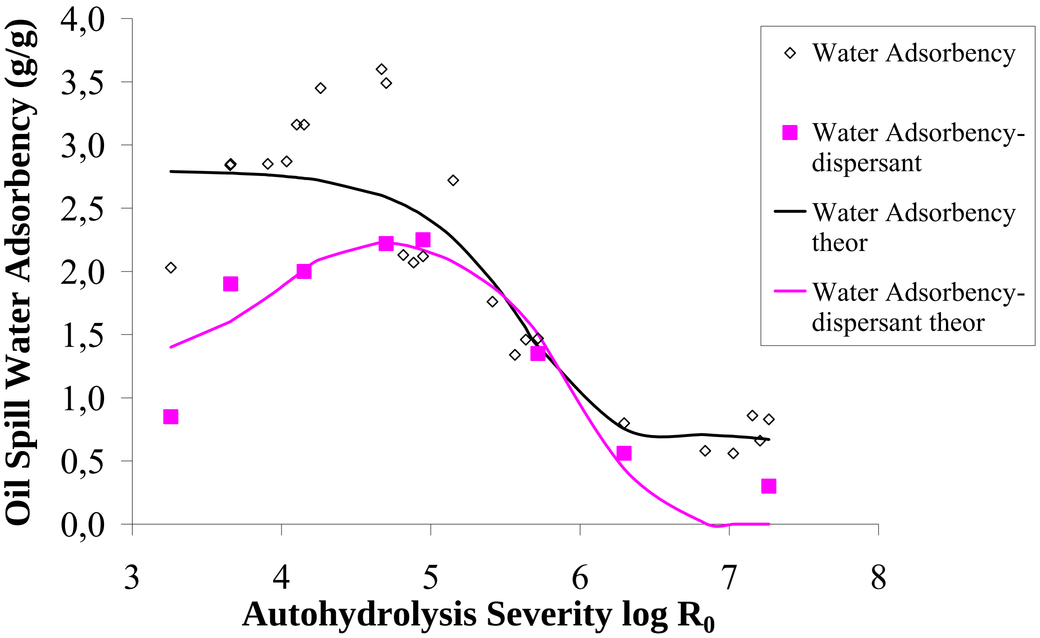


Fig. 10.13 UWS and AWS water adsorbency values vs. Severity Factor R_0 with and without the UOCD; the case of DOS on seawater

Diesel oil adsorbency and total adsorbency values with the UOCD (Figs 10.14 and 10.15) slightly decreased comparing to those of the wheat straw without the UOCD. Accordingly, RDA values with the UOCD (Fig. 10.16) presented no difference comparing to those of the wheat straw without the UOCD. Water, diesel oil and total adsorbency and RDA values of UWS and AWS in the cases of DOS on seawater with and without the UOCD are given in Table 10.7.

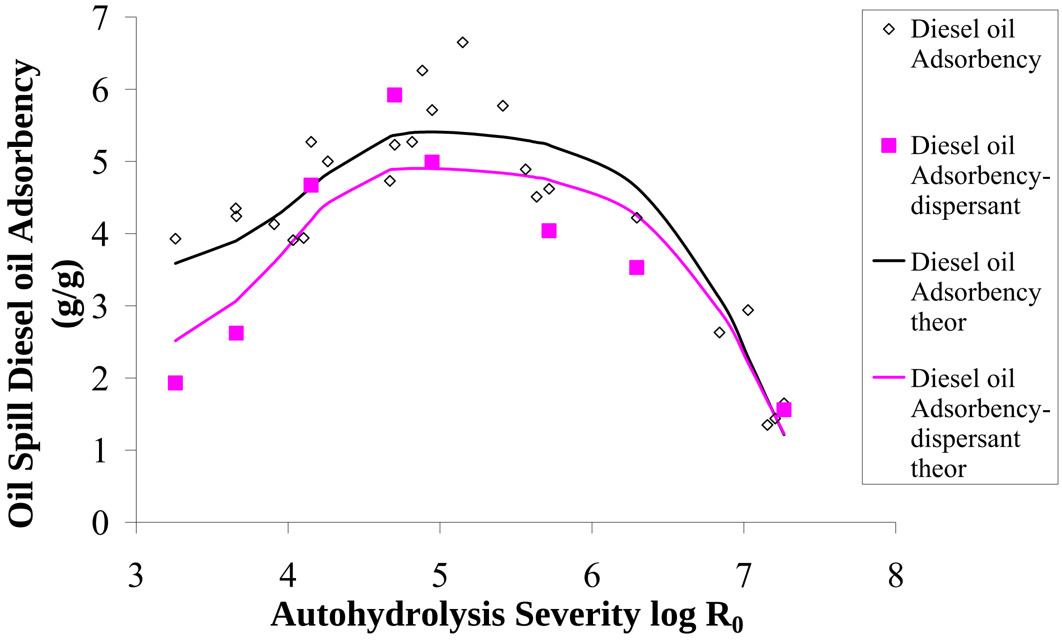


Fig. 10.14 UWS and AWS diesel oil adsorbency values vs. Severity Factor R_0 with and without the UOCD; the case of DOS on seawater

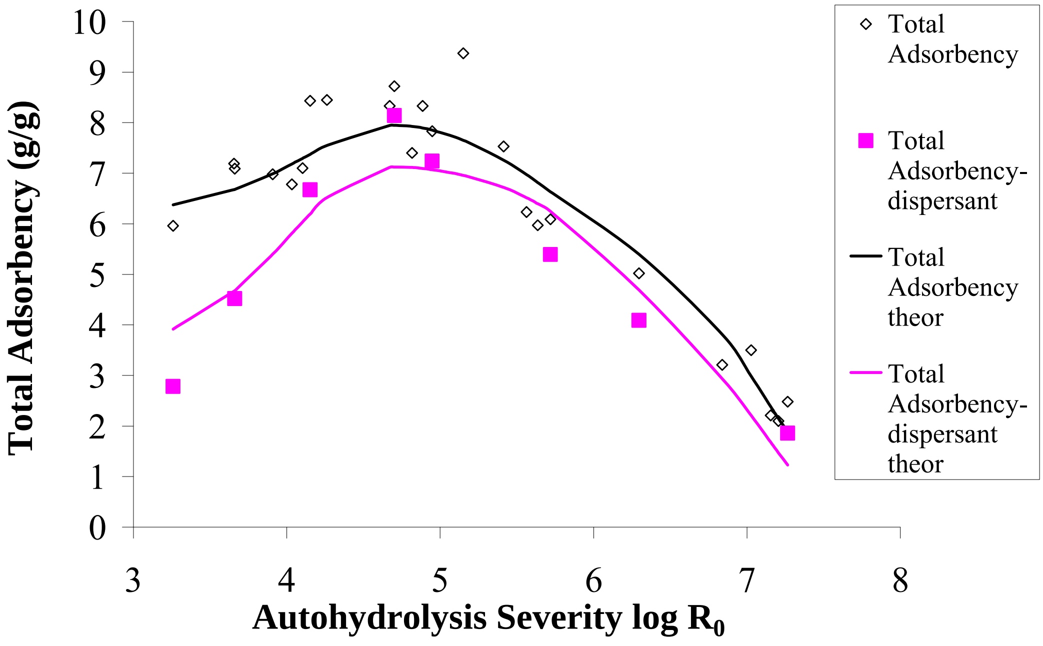


Fig. 10.15 UWS and AWS total adsorbency values vs. Severity Factor R_0 with and without the UOCD; the case of DOS on seawater

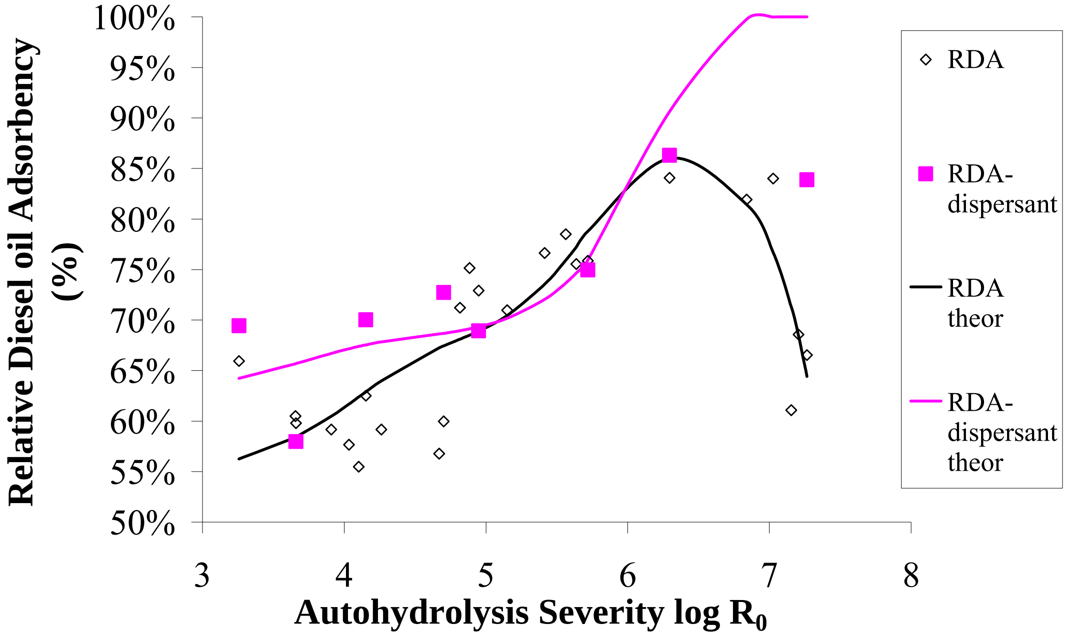
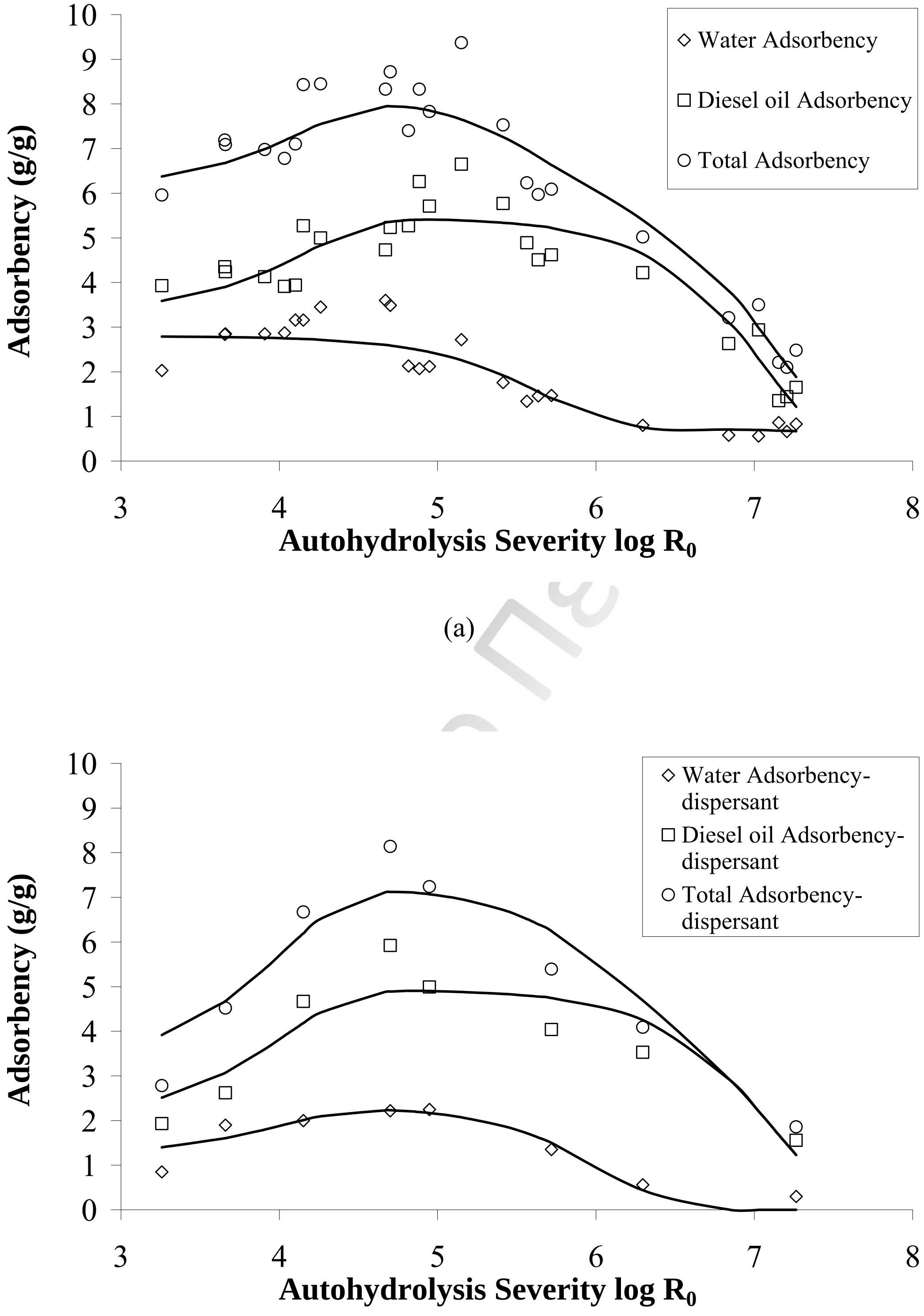


Fig. 10.16 UWS and AWS RDA values vs. Severity Factor R_0 with and without the UOCD; the case of DOS on seawater

The same conclusions derived from Fig. 10.17, where water adsorbency, diesel oil adsorbency and total adsorbency curves are shown in the case without the UOCD (Fig. 10.17a) and in the case with the UOCD (Fig. 10.17b).

Consequently, at the maximum adsorption points, as regards water adsorbency values in COS on seawater with the UOCD (Fig. 10.18) increased comparing to those of the wheat straw without the UOCD. Crude oil adsorbency values with the UOCD (Fig. 10.19) weren’t significantly different comparing to those of the wheat straw without the UOCD, while at the maximum adsorption points, total adsorbency values with the UOCD (Fig. 10.20) increased comparing to those of the wheat straw without the UOCD.

Finally, at the maximum adsorption points, RCA values with the UOCD (Fig. 10.21) decreased comparing to those of the wheat straw without the UOCD. The empirical constants’ values a_1, b_1, a_2, b_2 of UWS and AWS adsorbencies values with and without UOCD in the case of DOS on seawater were estimated using NLRA. These values and the SEE values are presented in Table 10.8.



(a)

(b)

Fig. 10.17 UWS and AWS adsorbencies values vs. Severity Factor R_0 (a) without and (b) with the UOCD; the case of DOS on seawater

Table 10.7 UWS and AWS adsorbencies values vs. Severity Factor R_0 with and without the UOCD; the case of DOS on seawater

T (°C)	t (min)	R_0	log R_0	SRY (%)	Water Adsorbency	Water Adsorbency with dispersant	Diesel oil Adsorbency	Diesel oil Adsorbency with dispersant	Total Adsorbency	Total Adsorbency with dispersant	RDA (%)	RDA (%) with dispersant
		$0.00\ 10^{0}$		100.0	0.88	1.51	2.76	2.71	3.64	4.22	75.8	64.2
160	0	$1.81\ 10^{3}$	3.26	90.0	2.03	0.85	3.93	1.93	5.96	2.78	65.9	69.4
160	10	$4.52\ 10^{3}$	3.66	88.2	2.84		4.35		7.19		60.5	
180	0	$4.57\ 10^{3}$	3.66	72.9	2.85	1.90	4.24	2.62	7.09	4.52	59.8	58.0
160	20	$8.09\ 10^{3}$	3.91	86.7	2.85		4.13		6.98		59.2	
160	30	$1.08\ 10^{4}$	4.03	84.6	2.87		3.91		6.78		57.7	
160	40	$1.26\ 10^{4}$	4.10	82.5	3.16		3.94		7.10		55.5	
160	50	$1.42\ 10^{4}$	4.15	80.0	3.16	2.00	5.27	4.67	8.43	6.67	62.5	70.0
180	10	$1.83\ 10^{4}$	4.26	63.7	3.45		5.00		8.45		59.2	
180	20	$4.68\ 10^{4}$	4.67	60.2	3.60		4.73		8.33		56.8	
200	0	$5.03\ 10^{4}$	4.70	53.0	3.49	2.22	5.23	5.92	8.72	8.14	60.0	72.7
180	30	$6.55\ 10^{4}$	4.82	56.7	2.13		5.27		7.40		71.2	
180	40	$7.67\ 10^{4}$	4.88	52.4	2.07		6.26		8.33		75.2	
180	50	$8.87\ 10^{4}$	4.95	51.1	2.12	2.25	5.71	4.99	7.83	7.24	72.9	68.9
200	10	$1.41\ 10^{5}$	5.15	51.9	2.72		6.65		9.37		71.0	
200	20	$2.59\ 10^{5}$	5.41	51.8	1.76		5.77		7.53		76.6	
200	30	$3.66\ 10^{5}$	5.56	50.9	1.34		4.89		6.23		78.5	
200	40	$4.33\ 10^{5}$	5.64	47.0	1.46		4.51		5.97		75.5	
200	50	$5.23\ 10^{5}$	5.72	42.5	1.47	1.35	4.62	4.04	6.09	5.39	75.9	75.0
240	0	$1.98\ 10^{6}$	6.30	45.5	0.80	0.56	4.22	3.53	5.02	4.09	84.1	86.3
240	10	$6.90\ 10^{6}$	6.84	40.2	0.58		2.63		3.21		81.9	
240	20	$1.06\ 10^{7}$	7.03	39.1	0.56		2.94		3.50		84.0	
240	30	$1.43\ 10^{7}$	7.15	37.3	0.86		1.35		2.21		61.1	
240	40	$1.61\ 10^{7}$	7.21	36.2	0.66		1.44		2.10		68.6	
240	50	$1.84\ 10^{7}$	7.27	33.9	0.83	0.30	1.65	1.56	2.48	1.86	66.5	83.9

The same conclusions derived from the study of Fig. 10.22, where water adsorbency, crude oil adsorbency and total adsorbency curves are shown in the case without the UOCD (Fig. 10.22a) and in the case with the UOCD (Fig. 10.22b). Water, crude oil and total adsorbency and RCA values of UWS and AWS in the cases of COS on seawater with and without the UOCD are given in Table 10.9.

Table 10.8 Simulation model parameters of UWS and AWS adsorbencies values with and without the UOCD; the case of DOS on seawater

Parameters	Water Adsorbency	Diesel oil Adsorbency	Water Adsorbency with dispersant	Diesel oil Adsorbency with dispersant
$a_1 = A'^{\infty} - A_0$	326.6	4504.8	251.5	6209.4
b_1	$4.76\ 10^{-9}$	$8.16\ 10^{-8}$	$8.46\ 10^{-7}$	$7.55\ 10^{-8}$
$a_2 = A_0$	2.798	3.345	1.235	2.061
b_2	$2.13\ 10^{-6}$	$6.75\ 10^{-5}$	$9.18\ 10^{-5}$	$9.51\ 10^{-5}$
sum	7.878	7.097	0.601	3.392
n'	25	25	9	9
p'	4	4	4	4
SEE	0.6125	0.5813	0.3466	0.8237

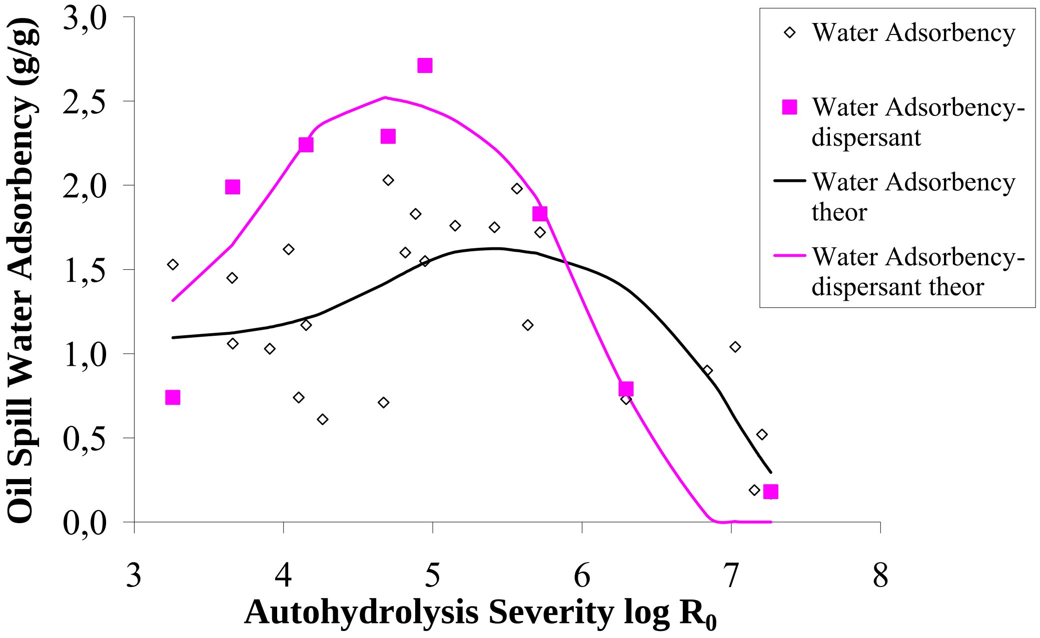


Fig. 10.18 UWS and AWS water adsorbency values vs. Severity Factor R_0 with and without the UOCD; the case of COS on seawater

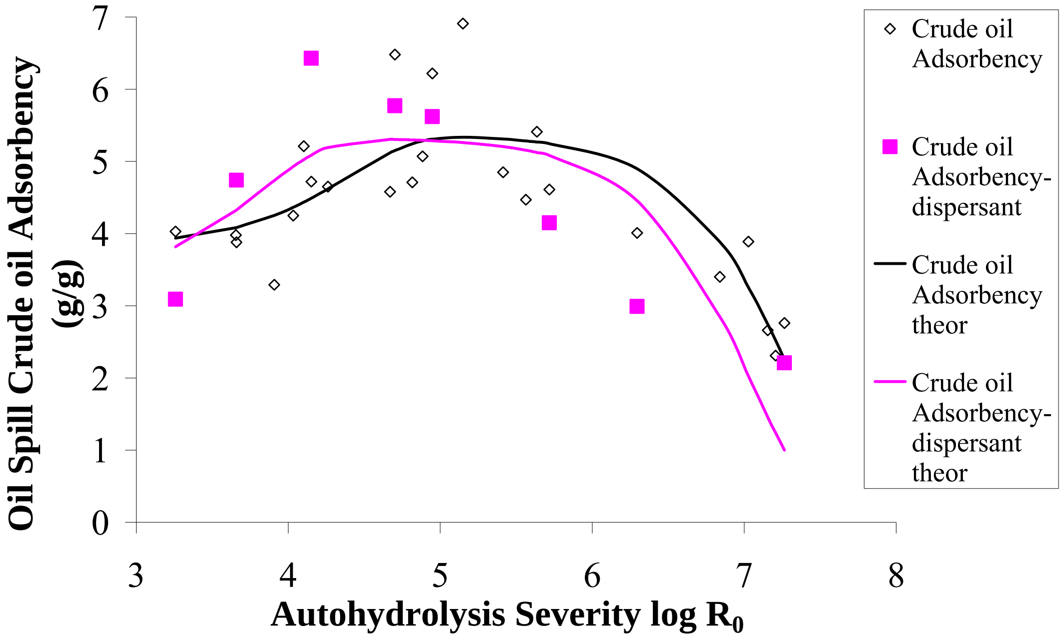


Fig. 10.19 UWS and AWS crude oil adsorbency values vs. Severity Factor R_0 with and without the UOCD; the case of COS on seawater

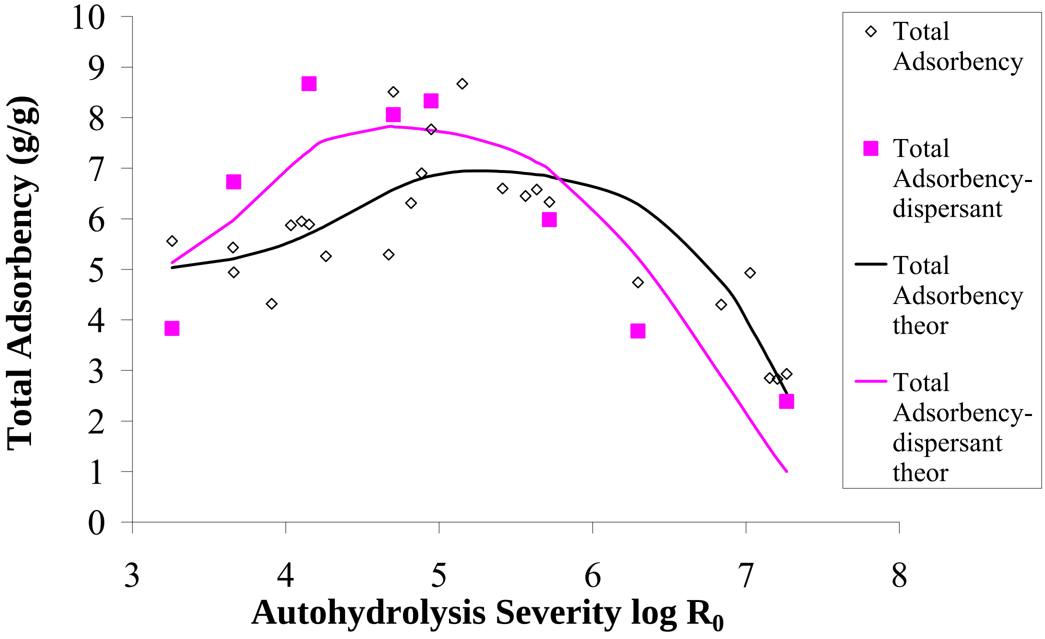


Fig. 10.20 UWS and AWS total adsorbency values vs. Severity Factor R_0 with and without the UOCD; the case of COS on seawater

Table 10.9 UWS and AWS adsorbencies values vs. Severity Factor R_0 with and without the UOCD; the case of COS on seawater

T (ºC)	*t* (min)	R_0	log R_0	SRY (%)	Water Adsorbency	Water Adsorbency with dispersant	Crude oil Adsorbency	Crude oil Adsorbency with dispersant	Total Adsorbency	Total Adsorbency with dispersant	RCA (%)	RCA (%) with dispersant
		$0.00\ 10^{0}$		100.0	0.94	1.30	4.08	3.53	5.02	4.83	81.3	73.1
160	0	$1.81\ 10^{3}$	3.26	90.0	1.53	0.74	4.03	3.09	5.56	3.83	72.5	80.7
160	10	$4.52\ 10^{3}$	3.66	88.2	1.45		3.98		5.43		73.3	
180	0	$4.57\ 10^{3}$	3.66	72.9	1.06	1.99	3.88	4.74	4.94	6.73	78.5	70.4
160	20	$8.09\ 10^{3}$	3.91	86.7	1.03		3.29		4.32		76.2	
160	30	$1.08\ 10^{4}$	4.03	84.6	1.62		4.25		5.87		72.4	
160	40	$1.26\ 10^{4}$	4.10	82.5	0.74		5.21		5.95		87.6	
160	50	$1.42\ 10^{4}$	4.15	80.0	1.17	2.24	4.72	6.43	5.89	8.67	80.1	74.2
180	10	$1.83\ 10^{4}$	4.26	63.7	0.61		4.65		5.26		88.4	
180	20	$4.68\ 10^{4}$	4.67	60.2	0.71		4.58		5.29		86.6	
200	0	$5.03\ 10^{4}$	4.70	53.0	2.03	2.29	6.48	5.77	8.51	8.06	76.1	71.6
180	30	$6.55\ 10^{4}$	4.82	56.7	1.60		4.71		6.31		74.6	
180	40	$7.67\ 10^{4}$	4.88	52.4	1.83		5.07		6.90		73.5	
180	50	$8.87\ 10^{4}$	4.95	51.1	1.55	2.71	6.22	5.62	7.77	8.33	80.1	67.5
200	10	$1.41\ 10^{5}$	5.15	51.9	1.76		6.91		8.67		79.7	
200	20	$2.59\ 10^{5}$	5.41	51.8	1.75		4.85		6.60		73.5	
200	30	$3.66\ 10^{5}$	5.56	50.9	1.98		4.47		6.45		69.3	
200	40	$4.33\ 10^{5}$	5.64	47.0	1.17		5.41		6.58		82.2	
200	50	$5.23\ 10^{5}$	5.72	42.5	1.72	1.83	4.61	4.15	6.33	5.98	72.8	69.4
240	0	$1.98\ 10^{6}$	6.30	45.5	0.73	0.79	4.01	2.99	4.74	3.78	84.6	79.1
240	10	$6.90\ 10^{6}$	6.84	40.2	0.90		3.40		4.30		79.1	
240	20	$1.06\ 10^{7}$	7.03	39.1	1.04		3.89		4.93		78.9	
240	30	$1.43\ 10^{7}$	7.15	37.3	0.19		2.66		2.85		93.3	
240	40	$1.61\ 10^{7}$	7.21	36.2	0.52		2.31		2.83		81.6	
240	50	$1.84\ 10^{7}$	7.27	33.9	0.17	0.18	2.76	2.21	2.93	2.39	94.2	92.5

The empirical constants' values a_1, b_1, a_2, b_2 of UWS and AWS adsorbencies values with and without the UOCD in the case of COS on seawater were estimated using NLRA. These values and the SEE values are presented in Table 10.10.

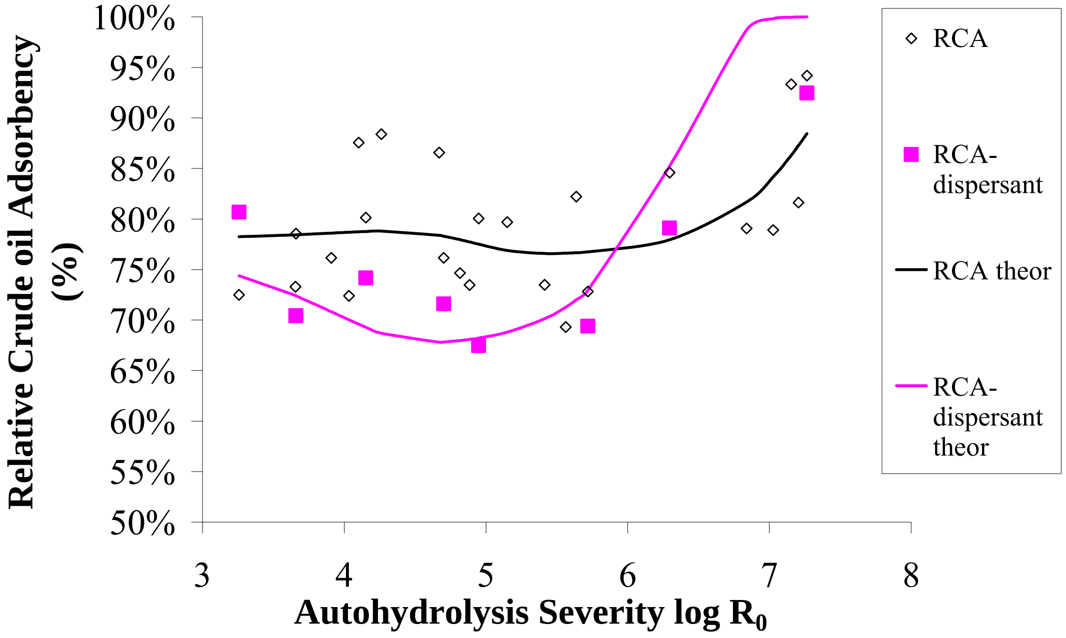
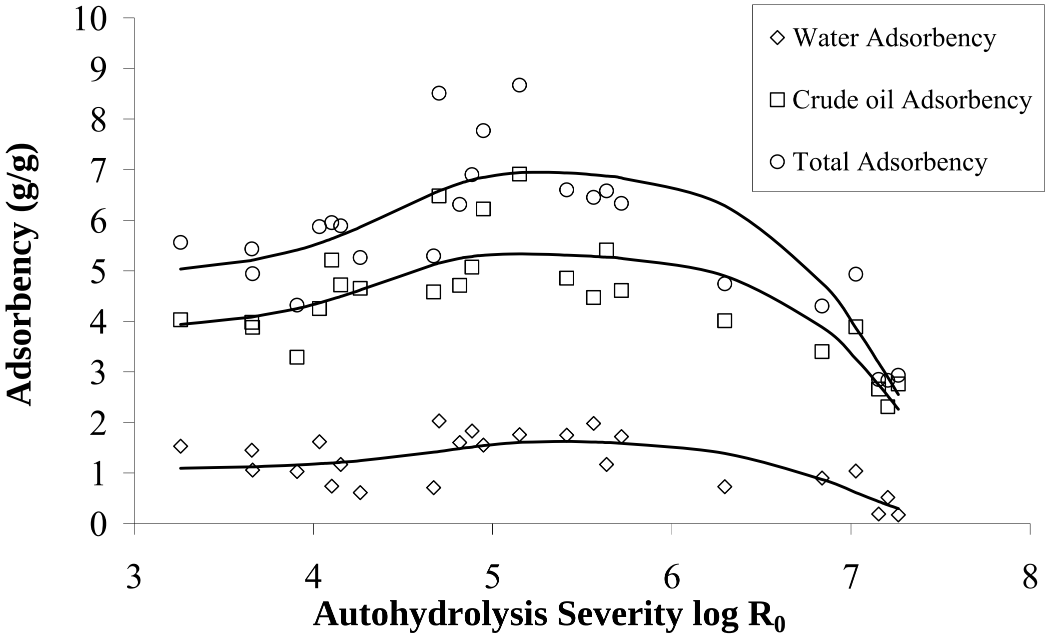


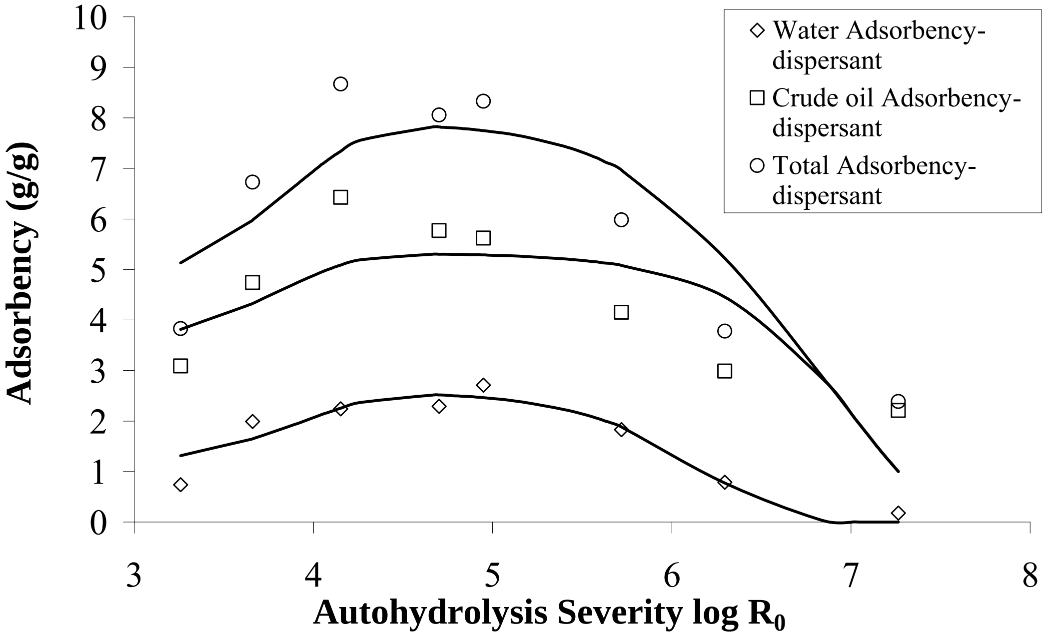
Fig. 10.21 UWS and AWS RCA values vs. Severity Factor R_0 with and without the UOCD; the case of COS on seawater

Table 10.10 Simulation model parameters of UWS and AWS adsorbencies values with and without the UOCD; the case of COS on seawater

Parameters	Water Adsorbency	Crude oil Adsorbency	Water Adsorbency with dispersant	Crude oil Adsorbency with dispersant
$a_1=A'\infty - A_0$	326.3	4504.8	467.9	8799.8
b_1	$9.42\ 10^{-8}$	$4.71\ 10^{-8}$	$6.15\ 10^{-7}$	$9.08\ 10^{-8}$
$a_2=A_0$	1.075	3.830	1.031	3.344
b_2	$1.85\ 10^{-5}$	$3.95\ 10^{-5}$	$1.11\ 10^{-4}$	$1.50\ 10^{-4}$
sum	3.201	10.444	0.666	7.337
n'	25	25	9	9
p'	4	4	4	4
SEE	0.3904	0.7052	0.3652	1.2113



(a)



(b)

Fig. 10.22 UWS and AWS adsorbencies values vs. Severity Factor R_0 (a) without and (b) with the UOCD; the case of COS on seawater

10.4 Effect of ageing on AWS adsorptivity

In this subchapter, the adsorption capacity of AWS at optimal conditions (180^{o}C for 50 min reaction time) in the case of pure liquids, COS and DOS on freshwater was examined. Then the same exactly sample was also examined for its adsorption capacity after one month and after one year of storage in plastic bag at room temperature and in absence of direct sunlight in order to determine the differences at the same conditions. Then statistical analysis, taking into account the experimental error resulting from the repeatability measurements, was done. The results are expected to show a reasonable degradation during storage and transportation of the adsorbent. This decrease can be attributed to the diminishing of free energy, according to the fundamental thermodynamic relation $\Delta G = \Delta H - T \cdot \Delta S$, where ΔG, ΔH, ΔS are the changes of free energy, enthalpy, and entropy, respectively. As a matter of fact, for constant absolute temperature T and ΔH, the entropy increases in order to obtain negative ΔG, which is the criterion for a transformation to occur spontaneously.

10.4.1 Pure liquids

The AWS was examined (initially, after one month and after one year) as regards its adsorption capacities on pure freshwater, diesel oil and crude oil. The results were thoroughly compared, to find out the influence of ageing on the adsorption capacity of the straw. After one month of ageing, AWS water adsorbency value was decreased from 12.02 g/g to 11.66 g/g. The ageing of this adsorption material was only 3.00%, although higher than the experimental error of the measurements which was 0.90-1.20%. AWS diesel oil adsorbency value was decreased from 4.38 g/g to 4.27 g/g. The ageing was only 2.40%, although higher than the experimental error of the measurements which was 1.70-2.00%. AWS crude oil adsorbency value was decreased from 6.71 g/g to 5.93 g/g. The ageing was 11.70%, significantly higher than the experimental error of the measurements which was 0.30-1.50%.

After one year of ageing, AWS's adsorption capacities were thoroughly decreased 10% approximately. In the Fig. 10.23 the decrease of pure water, diesel and crude oil adsorptivity (amount adsorbed) are shown as function of ageing time.

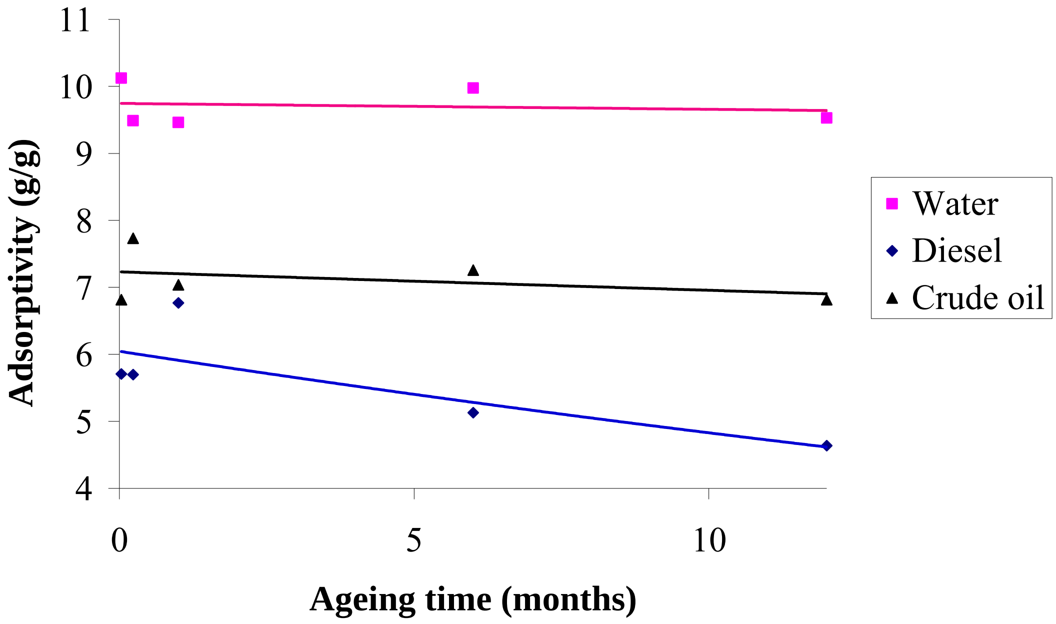


Fig. 10.23 AWS pure water/ diesel/ crude oil adsorptivity decrease due to ageing

10.4.2 Oil spill on freshwater

The AWS was examined (initially, after one month and after one year) as regards its adsorption capacities in the case of oil spills (DOS and COS) on freshwater. The results were thoroughly compared, to find out the influence of ageing on the adsorption capacity of the straw. After one month of ageing, in the case of DOS on freshwater, AWS water adsorbency value was decreased from 4.08 g/g to 3.09 g/g. The ageing of this adsorption material was 24.10%, as regards water adsorbency. Diesel oil adsorbency value was decreased from 4.84 g/g to 4.50 g/g. The ageing was 7.00%, as regards diesel oil adsorbency. RDA value was increased from 54.30% to 59.30%. There was no ageing effect as regards RDA value. Total adsorbency value was decreased from 8.92 g/g to 7.60 g/g. The ageing was 14.80% as regards Total Adsorbency. In the case of COS on freshwater, AWS water adsorbency value was decreased from 2.87 g/g to 2.45 g/g after one month of ageing. The ageing was 14.70%, as regards water adsorbency. Crude oil adsorbency value was decreased from 6.29 g/g to 5.75 g/g. The ageing was 8.50%, as regards crude oil adsorbency. RCA value was increased from 68.60% to 70.10%. There was no ageing effect as regards RCA value. Total adsorbency value was decreased from 9.16 g/g to 8.20 g/g. The ageing was 10.40%, as regards total adsorbency.

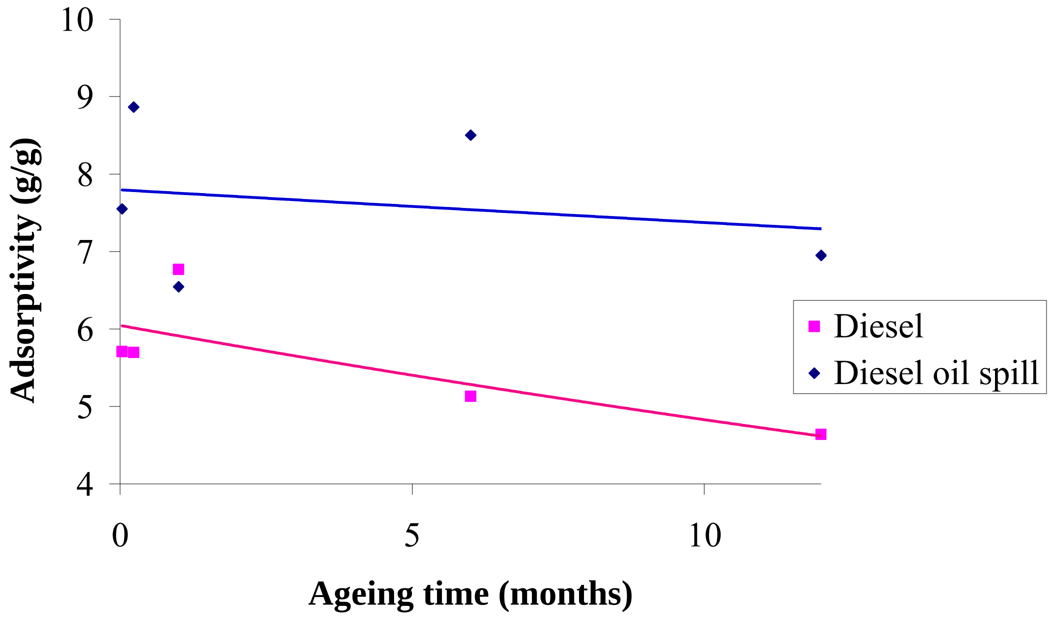


Fig. 10.24 AWS pure diesel/ diesel oil spill adsorptivity decrease due to ageing

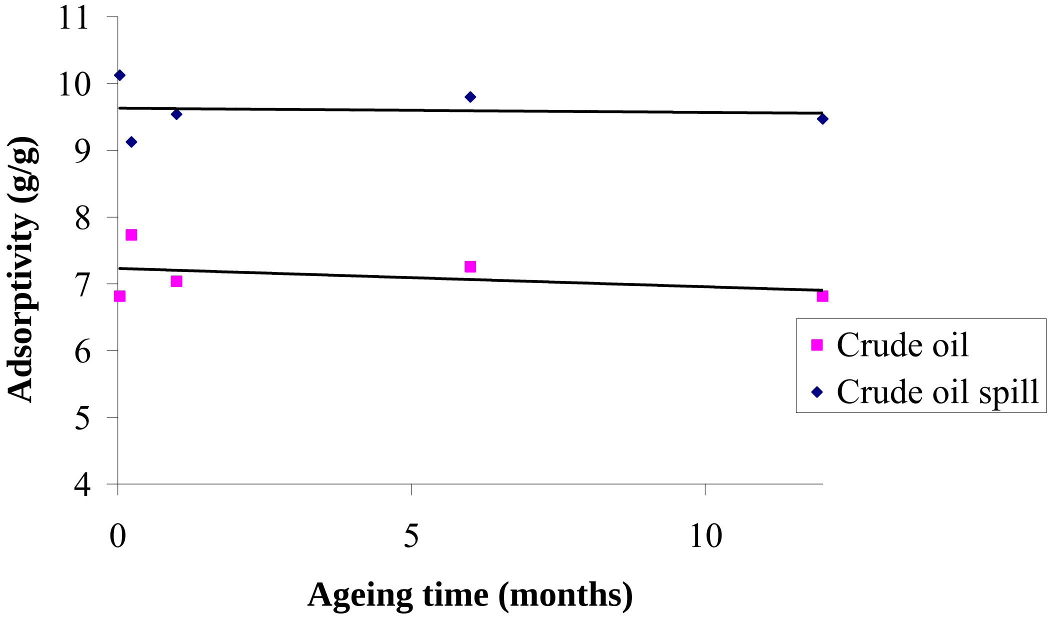


Fig. 10.25 AWS pure crude oil/ crude oil spill adsorptivity decrease due to ageing

After one year of ageing, AWS's adsorption capacities were thoroughly decreased 10% approximately. In the Figs 10.24 & 10.25 the decrease of diesel and crude oil adsorptivity (amount adsorbed) in the case of oil spills on freshwater are given as function of ageing time.

CHAPTER 11
KINETICS

11.1 Introduction

Several approaches have been reported in the literature and studies are in progress worldwide for developing cost-effective technologies using improved sorption materials for the removal of oil residuals from the oil-polluted water. The sorption kinetics which describes the solute sorption rate is an important characteristic in evaluating the efficiency of sorption (Thompson et al., 2010). The sorption procedure is usually studied by plotting the equilibrium concentration of a compound in the sorbent as a function of its equilibrium concentration in gas phase or in solution at given temperature.

Literature survey study shows that several sorption kinetic models of oils and other organic substances on several adsorbents describe the adsorption procedure. The ability of banana pseudostem fibers as a biosorbent for the removal of oil from synthetic oily wastewater was investigated to assess the feasibility of banana pseudostem fibers as sorbent for the removal of oil from oily wastewater (Husin et al., 2011). In their research the kinetic adsorption was analyzed by the Lagergren pseudo-first-order (Lagergren, 1898) and the second-order kinetic models (Ho et al., 2000). Nafaty et al., (2013), examined conditioned banana peel and tested it for oil uptake from produced water. In their study the kinetic adsorption was analyzed by the Lagergren pseudo-first-order, the second-order, the pseudo-second-order and the Elovich kinetic models (Eley, et al., 1970).

Uzunova et al., (2013), determined the influence of the bulk density on the sorption kinetics and efficiency of the sorbent, (pyrolyzed rice husks), for surface and emulsion contaminations. In their work the kinetic region of operation of the process was described, for both cases of sorption by different kinetic models, such as the Lagergren’s pseudo-first-order, the second order, the intraparticle diffusion (Weber and Morris, 1963) and the Elovich kinetic models.

Thompson et al., (2010), reported the sorption model and crude oil absorptive behavior of acetylated rice husks. They also studied the kinetics of the sorption procedure and the pseudo-second-order kinetic model was used to describe the method of sorption.

Bastani et al., (2006), examined four types of expanded perlite with different physical properties to adsorb oil spread on water surface. In their study kinetic studies for sorption of oil at ambient temperature using the expanded perlite were performed and the results obtained were correlated using the pseudo-first order, the pseudo-second order and the intra-particle diffusion models. Sathasivam and Haris, (2010), investigated modified banana trunk fibers (BTF) with oleic acid, stearic acid, castor oil, and palm oil, and evaluated the oil sorption capacity of the resulting fibrous materials. Their experimental data were analyzed using the pseudo-first-order and the pseudo-second-order adsorption kinetic models to determine the sorption kinetics of engine oil on BTF. Nwokoma and Anene, (2010), studied and evaluated the adsorption of crude oil from water using meshed groundnut shell as adsorbent. The kinetics of the crude oil adsorption onto meshed groundnut shell–adsorbent was analyzed using the pseudo-second-order kinetic model.

Sidik et al., (2012), evaluated the influence of surface modification on adsorption performance for the removal of crude oil under various experimental conditions of pH, adsorbent dosage, contact time, initial oil concentration and temperature. In their research they used the pseudo-first-order and the pseudo-second-order kinetic models to find the possible rate-controlling steps involved in the adsorption of crude oil. Gui et al., (2011), used highly porous carbon nanotube sponges as efficient sorbent materials for oil and organic reagent sorption. In their work the sorption process was described by the second-order kinetic model.

Finally, Syed et al., (2011), examined the effectiveness of a commercially available hydrophobic nano-silica as a sorbent for treating water contaminated with common automobile fuels, namely gasoline and diesel. In their research batch kinetic studies were carried out using the first-order and the second-order adsorption kinetic models.

11.2 Kinetic models

The kinetics of adsorption of oils (diesel and crude oil) on untreated and pretreated wheat straw has been extensively studied using mainly the following kinetic equations. The widely used Lagergren equation is shown below:

$$q - q_t = q \cdot e^{-k \cdot t} \tag{11.1}$$

where: q and q_t are the amounts of diesel or crude oil adsorbed quantity (in g) per g of untreated or pretreated wheat straw after equilibrium time ($t \to \infty$) and adsorption time t, respectively, while k is the pseudo-first order rate constant for the adsorption process (in $\min^{-1}$). Further modification of eq. (11.1) in logarithmic form gives:

$$ln(q - q_t) = ln\, q - k \cdot t \qquad (11.2)$$

The κ-order kinetic model is given by the following equation:

$$dq / dt = k_{\kappa}\left(q - q_t\right)^{\kappa} \qquad (11.3)$$

Solving this differential eq. for $\kappa \neq 1$, we obtain:

$$q_t = q - \left[q^{1-\kappa} + (\kappa - 1)k_{\kappa}t\right]^{1/(1-\kappa)} \qquad (11.4)$$

The commonly used second order kinetic model is as follows:

$$q_t = q - \left[q^{-1} + k_2 t\right]^{-1} \quad \text{or} \quad q_t = q - \frac{1}{\frac{1}{q} + k_2 t} \qquad (11.5)$$

The possibility of intra-particle diffusion was explored by using the intra-particle diffusion model, is given by the following equation:

$$q_t = c + k_p \cdot \sqrt{t} \qquad (11.6)$$

where: c is a constant (g g^{-1}) and k_p is the intra-particle diffusion rate constant in g g^{-1} $\min^{-0.5}$.

The Elovich or Roginsky–Zeldovich equation is generally expressed as follows (Low, 1960):

$$\frac{dq_t}{dt} = a \exp(-\beta q_t) \qquad (11.7)$$

where: q_t is the amount of oil adsorbed quantity (in g) per g of wheat straw after adsorption time t, α is the initial oil sorption rate (g g^{-1} $\min^{-1}$) and β is the desorption constant (g/g) during any one experiment. To simplify the Elovich equation, Chien and Clayton, (1980) assumed $\alpha\beta t >> 1$, and on applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, eq. (11.7) then becomes (Sparks, 1986):

$$q_t = \beta \ln(\alpha\beta) + \beta \ln t \quad \text{or} \quad q_t = A + \beta \ln t \qquad (11.8)$$

where: $A = \beta \ln(a\beta)$ and consequently $a = [\exp(A/\beta)]/\beta$.

Thus the constants can be obtained from the slope and intercept of the linear plot of q_t versus ln t. Eq. (11.8) will be used to test the applicability of the Elovich equation to the kinetics of oil sorption on to straw.

The fractional power function model is a modified form of the Freundlich equation and was used for soil phosphate desorption (Dalal, 1974) and for sorption of copper (II) on to peat (Ho and McKay, 2002). In this study, it was used for oil adsorption on to straw. This model can be expressed by eq. (11.9):

$$q_t = at^b \tag{11.9}$$

where: q_t is the amount of the adsorbate sorbed by the adsorbent at a time t, while a and b are constants with $b < 1$. Moreover, its linear form is given in eq. (11.10):

$$\ln q_t = \ln a + b \ln t \tag{11.10}$$

The one-parameter empirical kinetic model for diesel or crude oil adsorption on untreated or pretreated wheat straw is as follows:

$$q_t = q_{\exp}(1 - e^{-bt}) \tag{11.11}$$

where: qe_{xp} is diesel or crude oil adsorbed quantity (in g) per g of untreated or pretreated wheat straw after 24 hr and b is empirical parameter. Moreover, its linear form is given in eq. (11.12):

$$\ln\left(1 - \frac{q_t}{q_{\exp}}\right) = -bt \tag{11.12}$$

The two-parameter empirical kinetic model for diesel or crude oil adsorption on untreated or pretreated wheat straw is given by the following equation:

$$q_t = q_{\exp} - Ae^{-bt} \tag{11.13}$$

where: A, b are empirical parameters. Moreover, its linear form is given in eq. (11.14):

$$\ln(q_{\exp} - q_t) = \ln A - bt \tag{11.14}$$

The three-parameter empirical kinetic model for diesel or crude oil adsorption on untreated or pretreated wheat straw is shown below:

$$q_t = q - Ae^{-bt} \tag{11.15}$$

where: A, b, q are empirical parameters. Moreover, its linear form is given in eq. (11.16):

$$\ln(q - q_t) = \ln A - bt \tag{11.16}$$

11.3 Kinetic results of oil (diesel oil and crude oil) adsorption

In the following Tables, kinetic results of the triplicate adsorption rate batch experiments, in the cases: of diesel oil adsorption on UWS (Table 11.1), AWS (Table 11.2) and crude oil adsorption on UWS (Table 11.3), AWS (Table 11.4), were described.

Table 11.1 Kinetic results of diesel oil adsorption on UWS

t (min)	q_{t1}	q_{t2}	q_{t3}	q_t	stdev	stdev%
4	1.97	2.03	2.12	2.04	0.08	3.7%
7	2.21	2.07	2.12	2.14	0.07	3.2%
17	2.24	2.20	2.31	2.25	0.06	2.5%
32	2.19	2.32	2.33	2.28	0.08	3.5%
62	2.23	2.12	2.33	2.23	0.11	4.9%
122	2.29	2.33	2.31	2.31	0.02	0.9%
242	2.39	2.32	2.48	2.39	0.08	3.2%
1442	2.72	2.61	2.76	2.70	0.08	2.9%

Table 11.2 Kinetic results of diesel oil adsorption on AWS

t (min)	q_{t1}	q_{t2}	q_{t3}	q_t	stdev	stdev%
4	3.28	3.26	3.23	3.26	0.02	0.8%
7	3.23	3.17	3.21	3.20	0.03	1.0%
17	4.22	4.23	4.38	4.28	0.09	2.1%
32	3.57	3.63	3.70	3.63	0.06	1.7%
62	4.20	4.31	4.30	4.27	0.06	1.5%
122	4.83	4.76	4.79	4.79	0.04	0.8%
242	4.11	4.33	4.16	4.20	0.11	2.7%
1442	5.40	5.44	5.27	5.37	0.09	1.6%

Table 11.3 Kinetic results of crude oil adsorption on UWS

t (min)	q_{t1}	q_{t2}	q_{t3}	q_t	stdev	stdev%
4	2.68	2.58	2.60	2.62	0.05	2.1%
7	3.17	3.07	3.20	3.15	0.07	2.2%
17	3.58	3.48	3.57	3.54	0.06	1.6%
32	3.50	3.40	3.43	3.44	0.05	1.4%
62	3.42	3.38	3.44	3.42	0.03	0.9%
122	3.35	3.36	3.46	3.39	0.06	1.8%
242	3.63	3.59	3.71	3.64	0.06	1.7%
1442	4.30	4.33	4.39	4.34	0.04	1.0%

In the following Figures, oil adsorption on untreated and pretreated wheat straw is given vs. adsorption time t. All the above cases of the kinetic models were fitted to the experimental data. Moreover, in the accompanying Tables, the SEE and each kinetic model parameters' values (estimated using NLRA) are shown.

Table 11.4 Kinetic results of crude oil adsorption on AWS

t (min)	q_{t1}	q_{t2}	q_{t3}	q_t	stdev	stdev%
4	5.70	5.80	5.72	5.74	0.06	1.0%
7	6.40	6.52	6.43	6.45	0.06	0.9%
17	6.37	6.31	6.33	6.34	0.03	0.4%
32	6.78	6.74	6.66	6.73	0.06	1.0%
62	6.51	6.57	6.53	6.53	0.03	0.5%
122	6.47	6.56	6.54	6.53	0.05	0.7%
242	6.74	6.70	6.68	6.71	0.03	0.5%
1442	7.41	7.34	7.38	7.38	0.03	0.5%

The standard error of estimates (SEE)-values (g/g), were calculated by the following equation:

$$\text{SEE} = \sqrt{\sum_{i=1}^{n'} (y_i - y_{i,theor})^2 / (n' - p')} \tag{11.17}$$

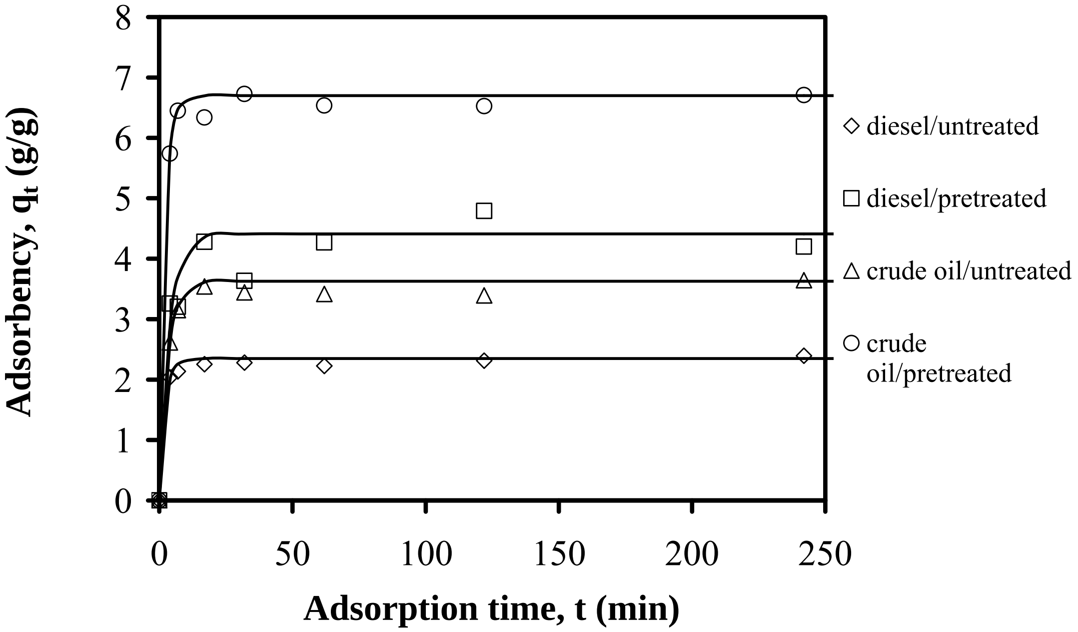
where: y_i is the experimental value of the depended variable, $y_{i,theor}$ is the theoretical (estimated) value of the depended variable, n' is the number of the experimental measurements and p' is the number of parameters, i.e., $(n' - p')$ is the number of the degrees of freedom. It must be mentioned that sum is the sum of squares of the error of estimate.

Table 11.5 First order kinetic model parameter values for oil adsorption on untreated and pretreated wheat straw

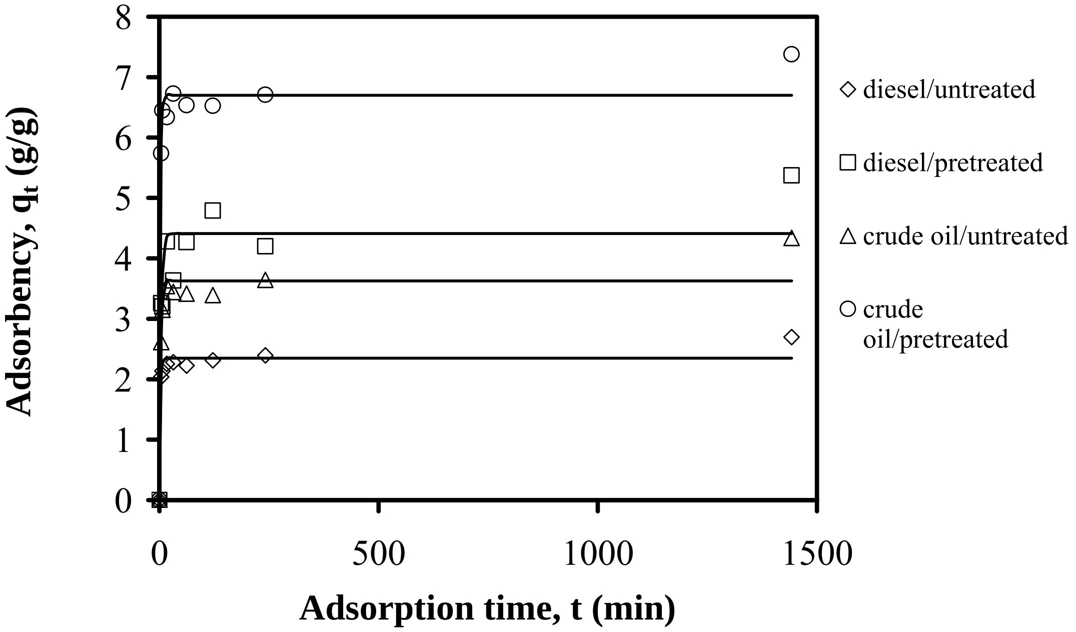
Case	Diesel/UWS	Diesel/AWS	Crude oil/UWS	Crude oil/AWS
sum	0.1701	2.1463	0.6527	0.6488
n'	9	9	9	9
p'	2	2	2	2
SEE	0.1559	0.5537	0.3054	0.3044
k	0.4654	0.2595	0.3078	0.4824
q	2.35	4.41	3.63	6.70

In Fig. 11.1, oil adsorption on wheat straw is given vs. adsorption time. In Fig. 11.1(a) and (b) the time range is t<250 min and t<1500 min respectively.

The model fitted in this case is the first order kinetic model. Finally, in Table 11.5 the estimated values of sum, n’, p’, SEE and k, q are presented.

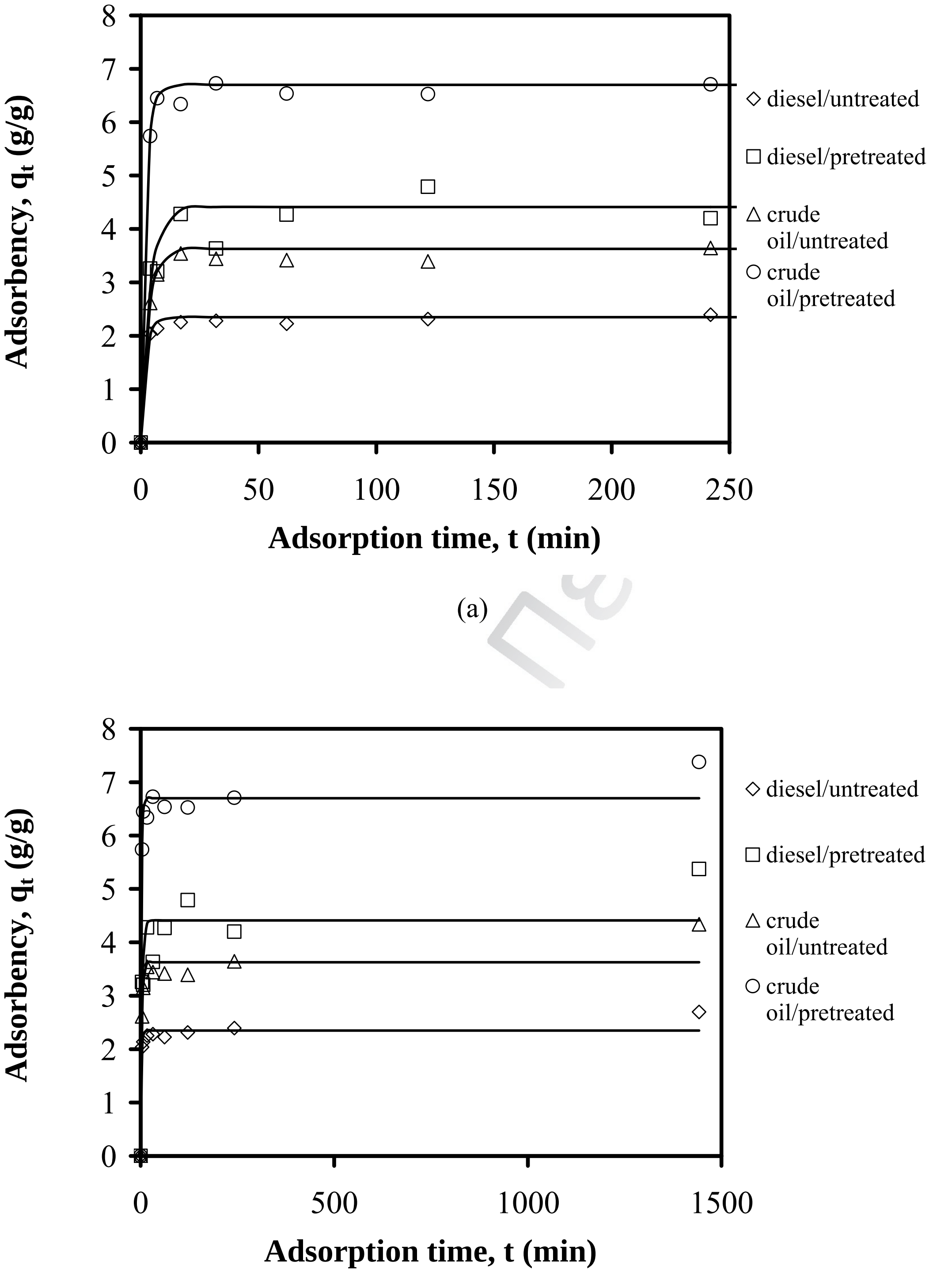


(a)



(b)

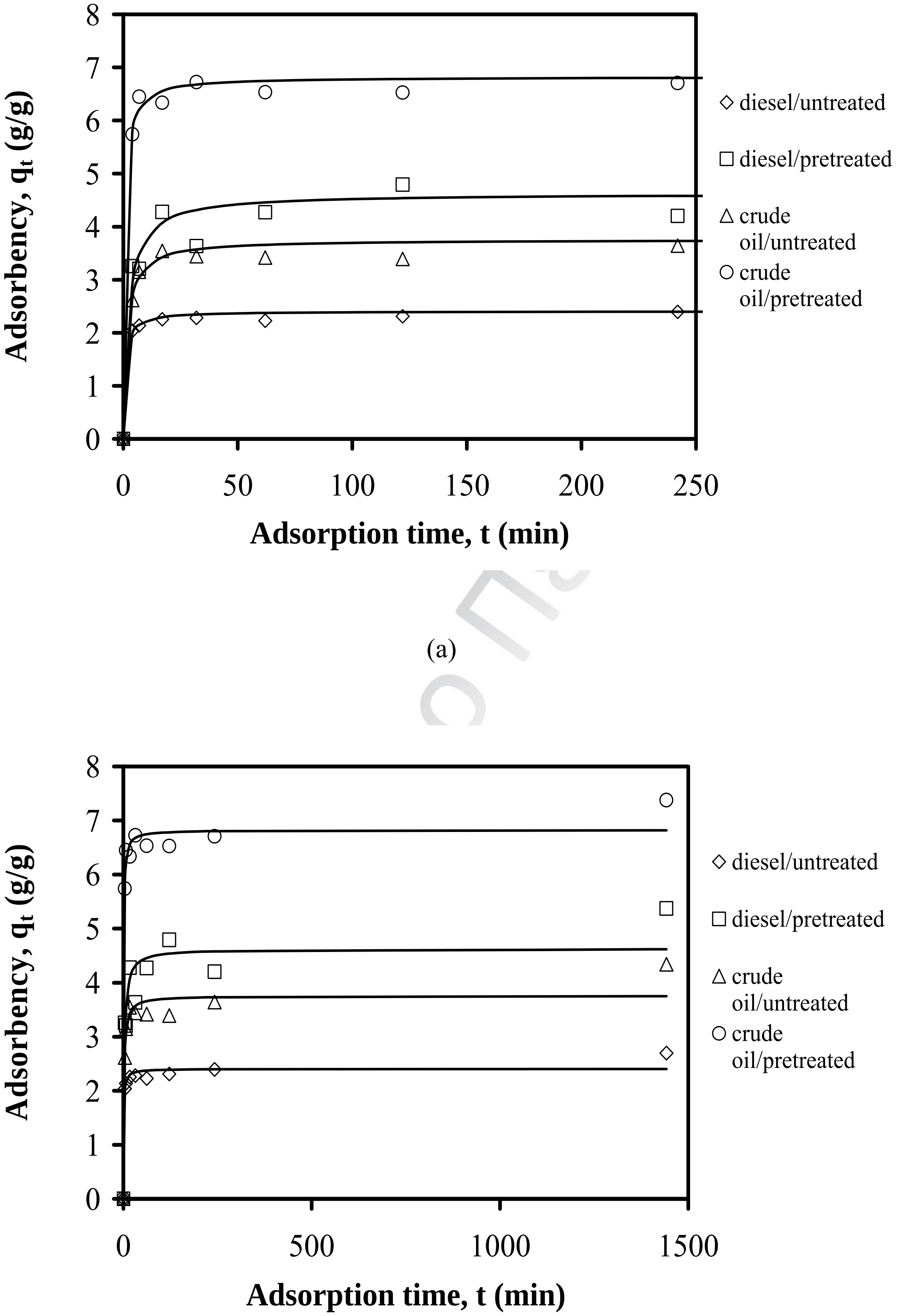
Fig. 11.1 Oil adsorbency for untreated and pretreated wheat straw vs. adsorption time: (a) for *t*<250 min and (b) for *t*<1500 min; first order kinetic model was applied



(a)

(b)

Fig. 11.2 Oil adsorbency for untreated and pretreated wheat straw vs. adsorption time: (a) for *t*<250 min and (b) for *t*<1500 min; first order kinetic model with fixed kernel was applied



(a)

(b)

Fig. 11.3 Oil adsorbency for untreated and pretreated wheat straw vs. adsorption time: (a) for *t*<250 min and (b) for *t*<1500 min; second order kinetic model was applied

Table 11.6 First order kinetic model with fixed kernel parameter values for oil adsorption on untreated and pretreated wheat straw

Case	Diesel/UWS	Diesel/AWS	Crude oil/UWS	Crude oil/AWS
sum	0.1700	2.1422	0.6527	0.6488
n’	9	9	9	9
p’	3	3	3	3
SEE	0.1683	0.5975	0.3298	0.3288
c	0.0036	0.0650	0.0064	0.0009
k	0.4650	0.2558	0.3074	0.4823
q	2.35	4.41	3.63	6.70

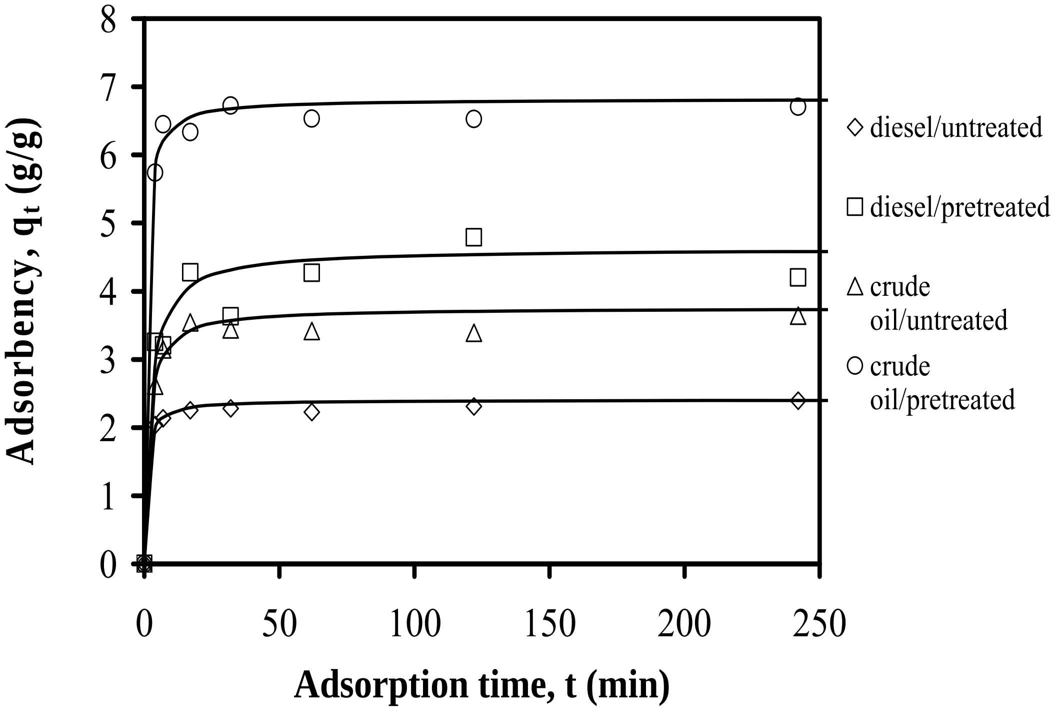
In Figs. 11.2 and 11.3, oil adsorption on UWS/ AWS vs. adsorption time t: (a) for t<250 min and (b) for t<1500 min in the cases of the first order with fixed kernel and of the second order kinetic models were shown, respectively, while in Tables 11.6 and 11.7, sum, n’, p’, SEE, c, k, q values and sum, n’, p’, SEE, k_2, q values were performed, respectively.

Table 11.7 Second order kinetic model parameter values for oil adsorption on untreated and pretreated wheat straw

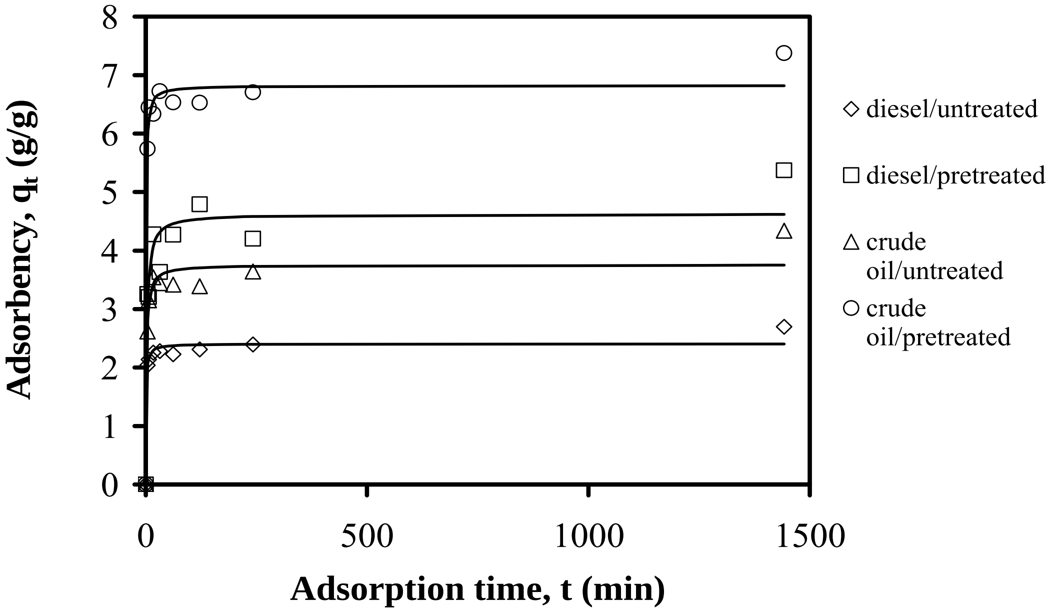
Case	Diesel/UWS	Diesel/AWS	Crude oil/UWS	Crude oil/AWS
sum	0.1206	1.4970	0.5563	0.5465
n’	9	9	9	9
p’	2	2	2	2
SEE	0.1313	0.4624	0.2819	0.2794
k_2	0.4993	0.0935	0.1629	0.2107
q	2.40	4.62	3.75	6.82

Table 11.8 Second order kinetic model with fixed kernel parameter values for oil adsorption on untreated and pretreated wheat straw

Case	Diesel/UWS	Diesel/AWS	Crude oil/UWS	Crude oil/AWS
sum	0.1206	1.4962	0.5563	0.5465
n’	9	9	9	9
p’	3	3	3	3
SEE	0.1418	0.4994	0.3045	0.3018
c	0.0011	0.0271	0.0002	0.0001
k_2	0.4992	0.0932	0.1629	0.2107
q	2.40	4.62	3.75	6.82



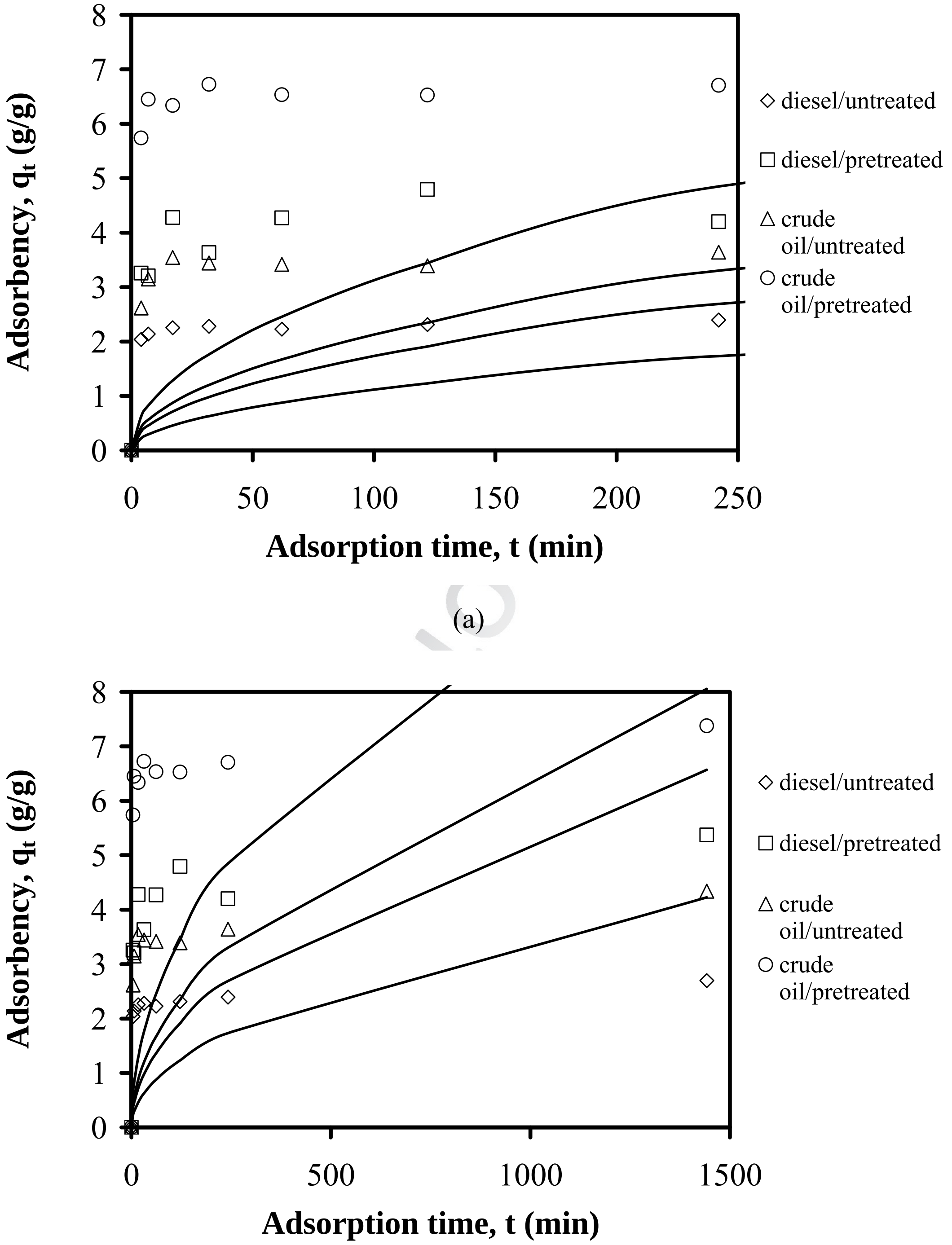
(a)



(b)

Fig. 11.4 Oil adsorbency for untreated and pretreated wheat straw vs. adsorption time: (a) for t<250 min and (b) for t<1500 min; second order kinetic model with fixed kernel was applied

In Fig. 11.4, oil adsorption on wheat straw vs. adsorption time t: (a) for t<250 min and (b) for t<1500 min in the case of the second order kinetic model with fixed kernel was shown, while in Table 11.8 sum, n', p', SEE and c, k_2, q values were performed.



(a)

(b)

Fig. 11.5 Oil adsorbency for untreated and pretreated wheat straw vs. adsorption time: (a) for *t*<250 min and (b) for *t*<1500 min; intra-particle diffusion kinetic model was applied

Table 11.9 Intra-particle diffusion kinetic model parameter values for oil adsorption on untreated and pretreated wheat straw

Case	Diesel/UWS	Diesel/AWS	Crude oil/UWS	Crude oil/AWS
sum	18.4104	53.2706	38.7608	157.4402
n’	9	9	9	9
p’	1	1	1	1
SEE	1.5170	2.5805	2.2012	4.4362
k_p	0.1113	0.2122	0.1730	0.3116

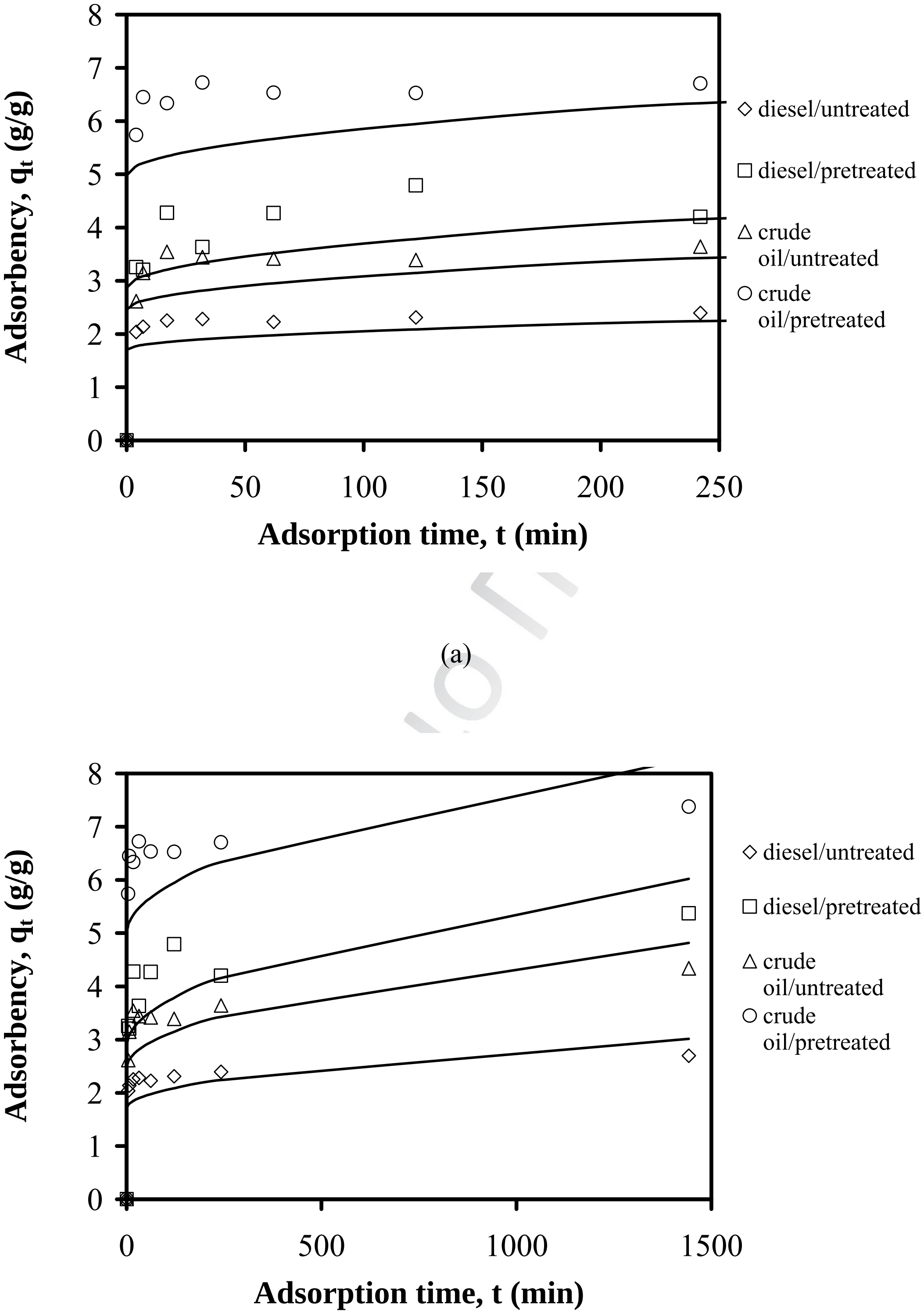
In Fig. 11.5, oil adsorption on wheat straw vs. adsorption time t: (a) for t<250 min and (b) for t<1500 min in the case of the intra-particle diffusion kinetic model was shown, while in Table 11.9 sum, n’, p’, SEE and k_p values were performed. In Fig. 11.6, oil adsorption on wheat straw vs. adsorption time t: (a) for t<250 min and (b) for t<1500 min in the case of the intra-particle diffusion kinetic model with fixed kernel was shown, while in Table 11.10 sum, n’, p’, SEE and c, k_p values were performed. In Figs 11.7 and 11.8, oil adsorption on wheat straw vs. adsorption time in logarithmic form and vs. adsorption time t: (a) for t<250 min and (b) for t<1500 min in the case of the Elovich kinetic model were shown respectively, while in Table 11.11 sum, n’, p’, SEE and A, β, α values were performed.

Table 11.10 Intra-particle diffusion kinetic model with fixed kernel parameter values for oil adsorption on untreated and pretreated wheat straw

Case	Diesel/UWS	Diesel/AWS	Crude oil/UWS	Crude oil/AWS
sum	3.6406	11.5078	7.9637	31.3052
n’	9	9	9	9
p’	2	2	2	2
SEE	0.7212	1.2822	1.0666	2.1148
c	1.7042	2.8657	2.4609	4.9803
k_p	0.0345	0.0831	0.0621	0.0872

Table 11.11 Elovich kinetic model parameter values for oil adsorption on untreated and pretreated wheat straw

Case	Diesel/UWS	Diesel/AWS	Crude oil/UWS	Crude oil/AWS
sum	0.0271	0.8062	0.3288	0.3417
n’	8	8	8	8
p’	2	2	2	2
SEE	0.0672	0.3666	0.2341	0.2386
A	1.9162	2.7829	2.5716	5.7430
β	0.0960	0.3430	0.2225	0.2060
α	$4.87\ 10^{9}$	$9.72\ 10^{3}$	$4.71\ 10^{5}$	$6.22\ 10^{12}$



(a)

(b)

Fig. 11.6 Oil adsorbency for untreated and pretreated wheat straw vs. adsorption time: (a) for *t*<250 min and (b) for *t*<1500 min; intra-particle diffusion kinetic model with fixed kernel was applied

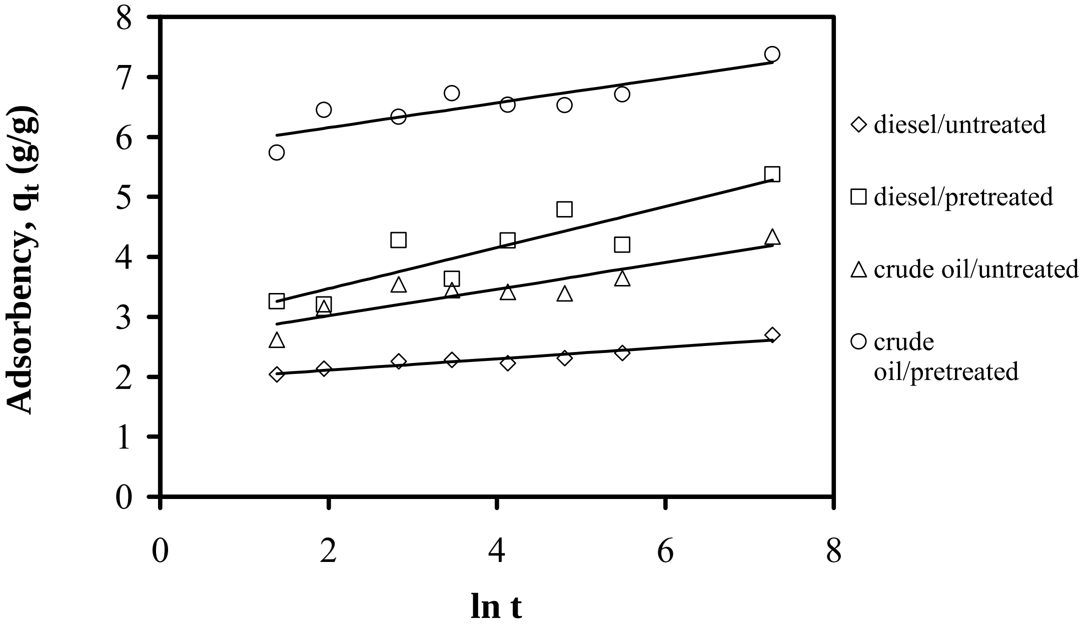
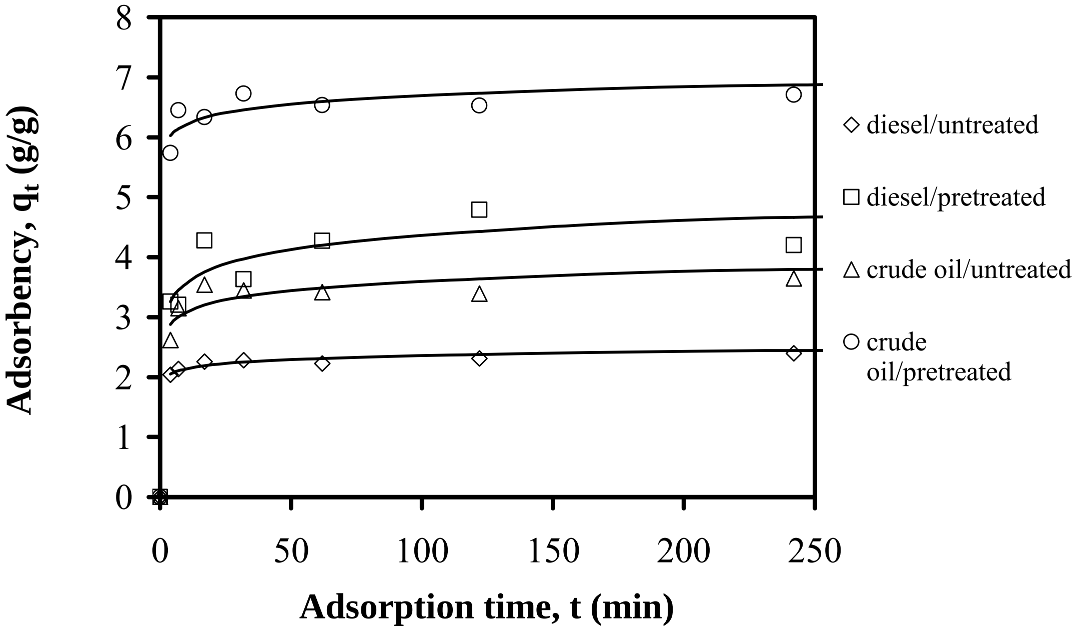
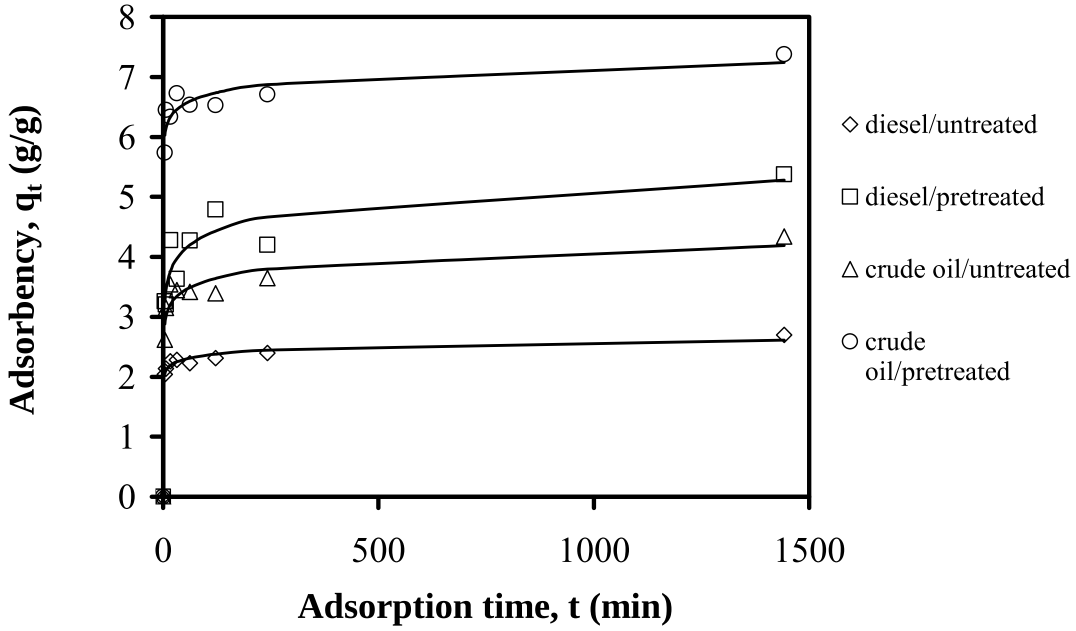


Fig. 11.7 Oil adsorbency for untreated and pretreated wheat straw vs. adsorption time in logarithmic form



(a)



(b)

Fig. 11.8 Oil adsorbency for untreated and pretreated wheat straw vs. adsorption time: (a) for t<250 min and (b) for t<1500 min; Elovich kinetic model was applied

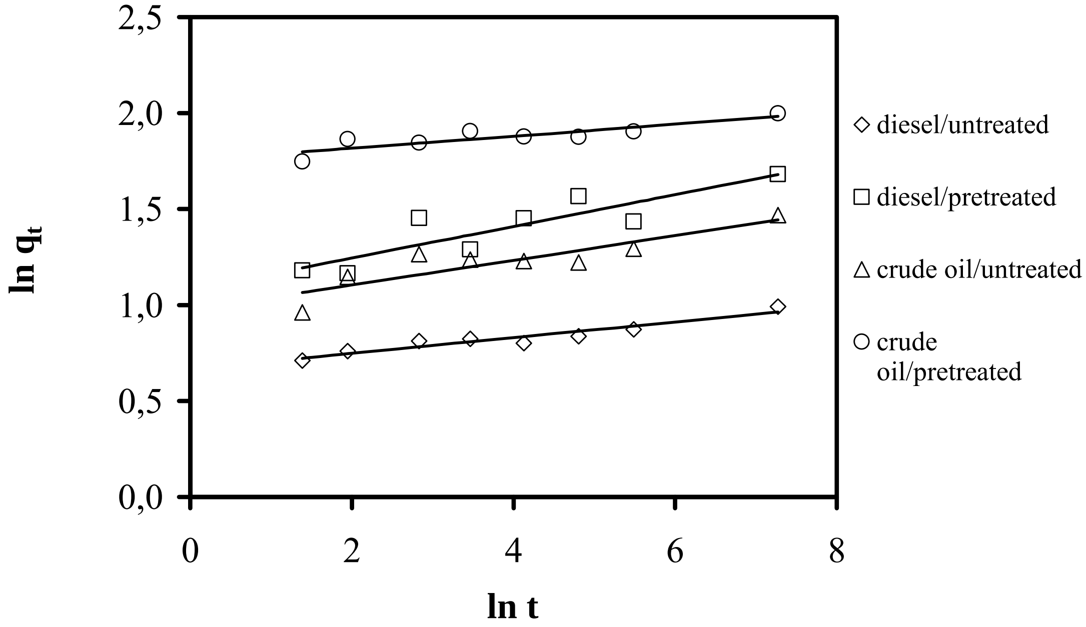
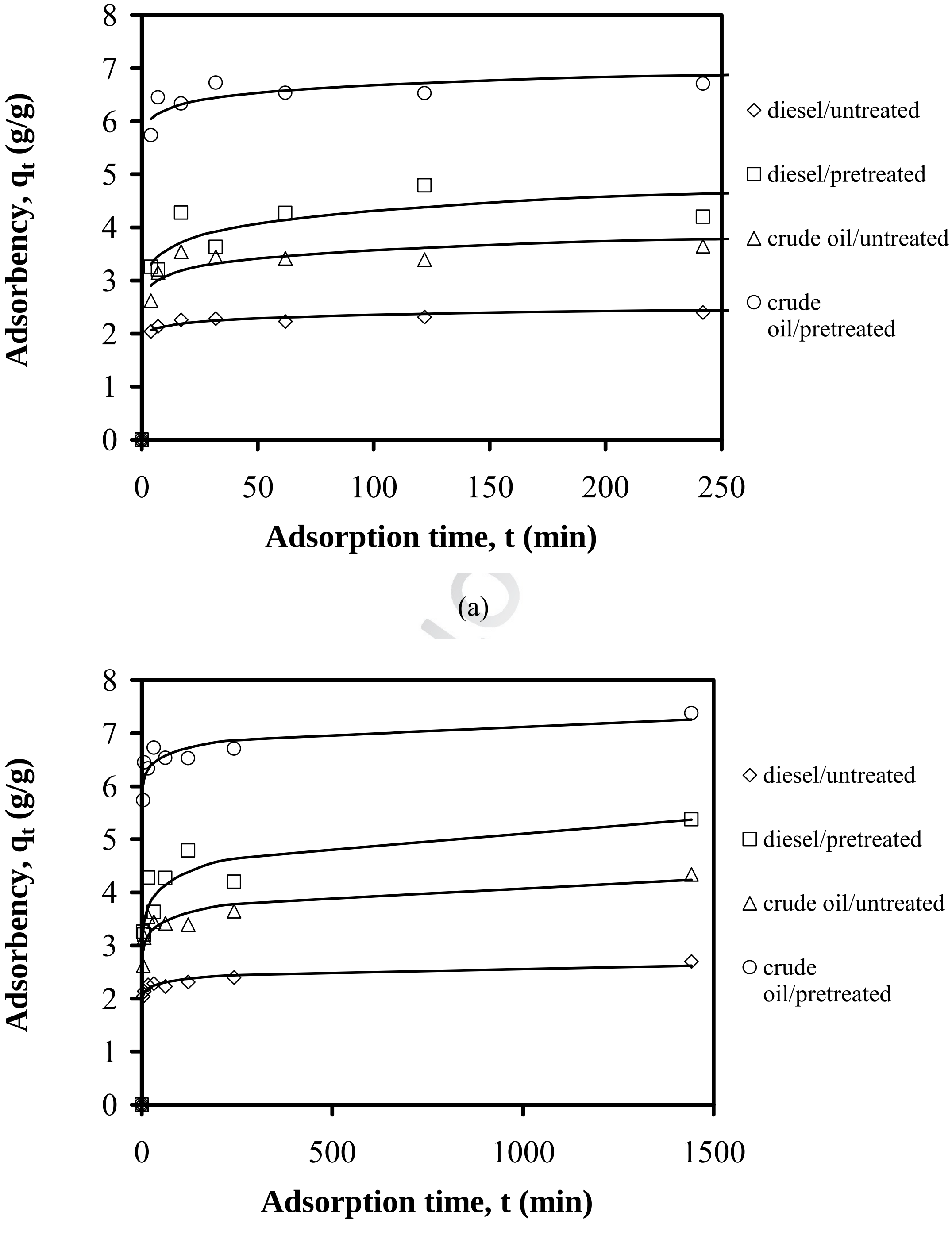


Fig. 11.9 Oil adsorbency in logarithmic form for untreated and pretreated wheat straw vs. adsorption time in logarithmic form

In Figs 11.9 and 11.10, oil adsorption on wheat straw vs. adsorption time in logarithmic form and vs. adsorption time t: (a) for t<250 min and (b) for t<1500 min in the case of the fractional power function kinetic model were shown respectively, while in Table 11.12 sum, n’, p’, SEE and ln a, b, a values were performed.



(a)

(b)

Fig. 11.10 Oil adsorbency for untreated and pretreated wheat straw vs. adsorption time: (a) for *t*<250 min and (b) for *t*<1500 min; fractional power function kinetic model was applied

Table 11.12 Fractional power function kinetic model parameter values for oil adsorption on untreated and pretreated wheat straw

Case	Diesel/UWS	Diesel/AWS	Crude oil/UWS	Crude oil/AWS
sum	0.0044	0.0497	0.0317	0.0085
n’	8	8	8	8
p’	2	2	2	2
SEE	0.0270	0.0911	0.0726	0.0375
ln a	0.6664	1.0792	0.9753	1.7546
b	0.0409	0.0827	0.0644	0.0313
a	1.95	2.94	2.65	5.78

In Fig. 11.11, oil adsorption on wheat straw vs. adsorption time t: (a) for t<250 min and (b) for t<1500 min in the case of the one-parameter empirical kinetic model was shown, while in Table 11.13 sum, n’, p’, SEE and b, q_{exp} values were performed.

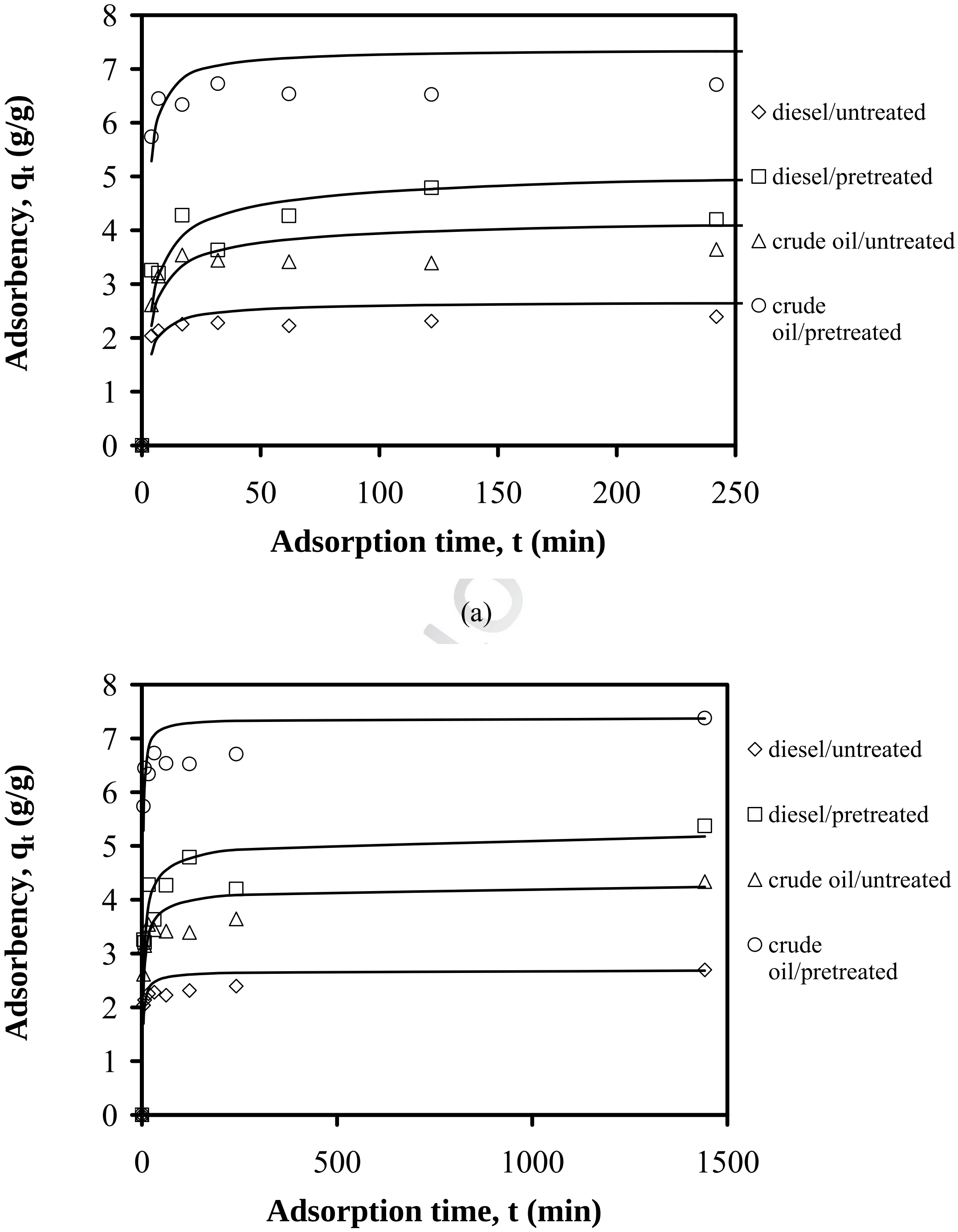
Table 11.13 One-parameter empirical kinetic model parameter values for oil adsorption on untreated and pretreated wheat straw

Case	Diesel/UWS	Diesel/AWS	Crude oil/UWS	Crude oil/AWS
sum	0.4302	1.7466	1.1050	2.0630
n’	8	8	8	8
p’	1	1	1	1
SEE	0.2479	0.4995	0.3973	0.5429
b	0.7144	0.4546	0.5178	0.9093
q_{exp}	2.70	5.37	4.34	7.38

Table 11.14 Two-parameter empirical kinetic model parameter values for oil adsorption on untreated and pretreated wheat straw

Case	Diesel/UWS	Diesel/AWS	Crude oil/UWS	Crude oil/AWS
sum	0.0527	0.9521	0.3851	0.3903
n’	8	8	8	8
p’	2	2	2	2
SEE	0.0937	0.3984	0.2534	0.2550
A	0.9062	3.3230	2.2086	2.0423
b	0.2234	0.2774	0.2536	0.2543
q_{exp}	2.70	5.37	4.34	7.38

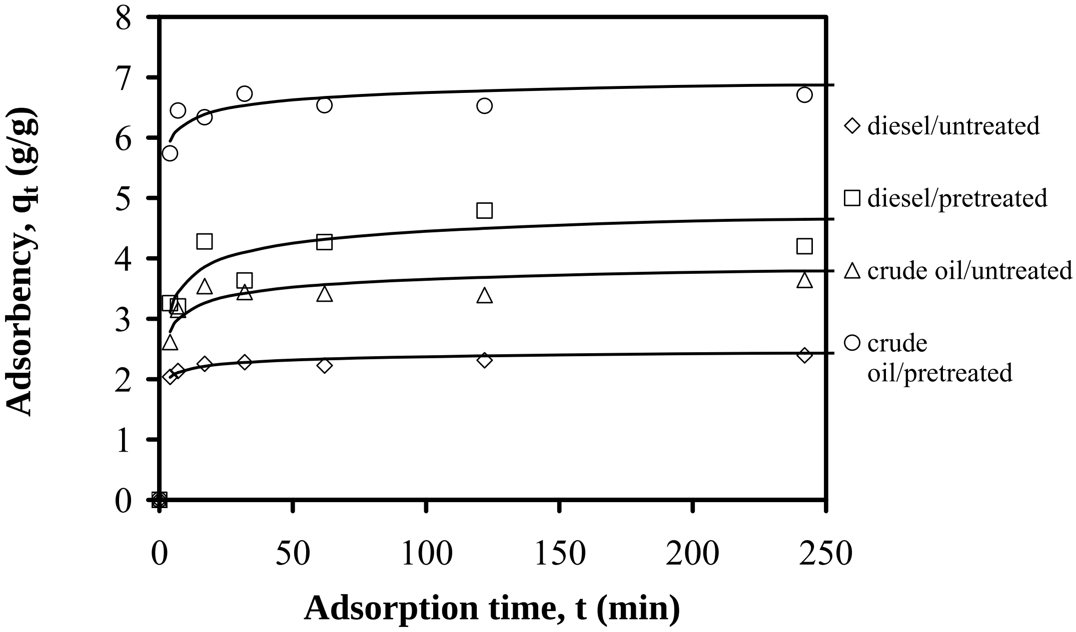
In Fig. 11.12, oil adsorption on wheat straw vs. adsorption time t: (a) for t<250 min and (b) for t<1500 min in the case of the two-parameter empirical kinetic model was shown, while in Table 11.14 sum, n’, p’, SEE and A, b, q_{exp} values were performed.



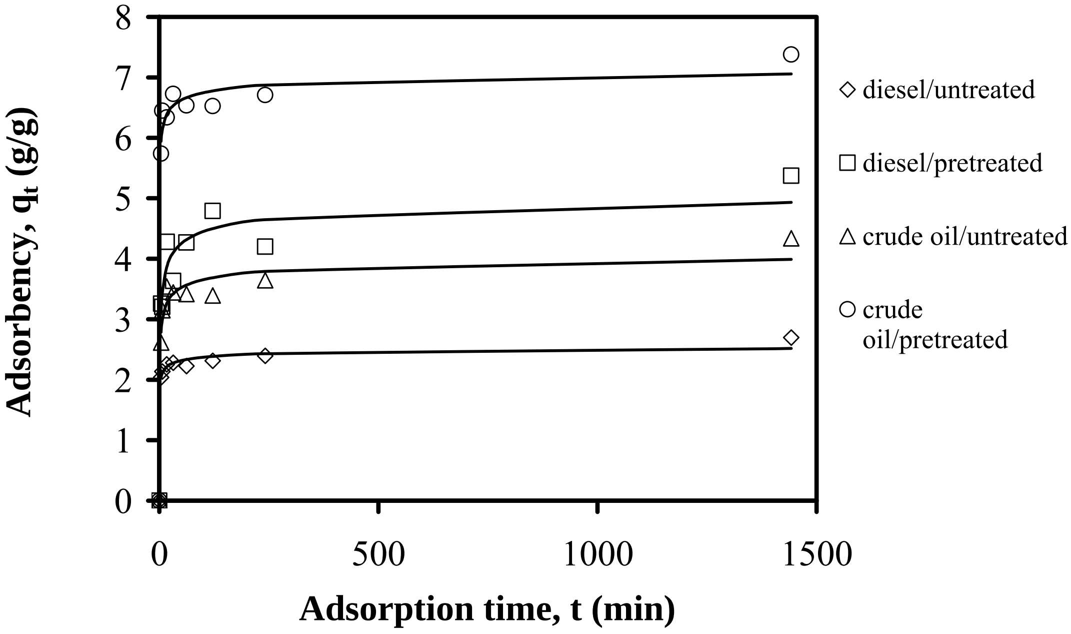
(a)

(b)

Fig. 11.11 Oil adsorbency for untreated and pretreated wheat straw vs. adsorption time: (a) for *t*<250 min and (b) for *t*<1500 min; one-parameter empirical kinetic model was applied

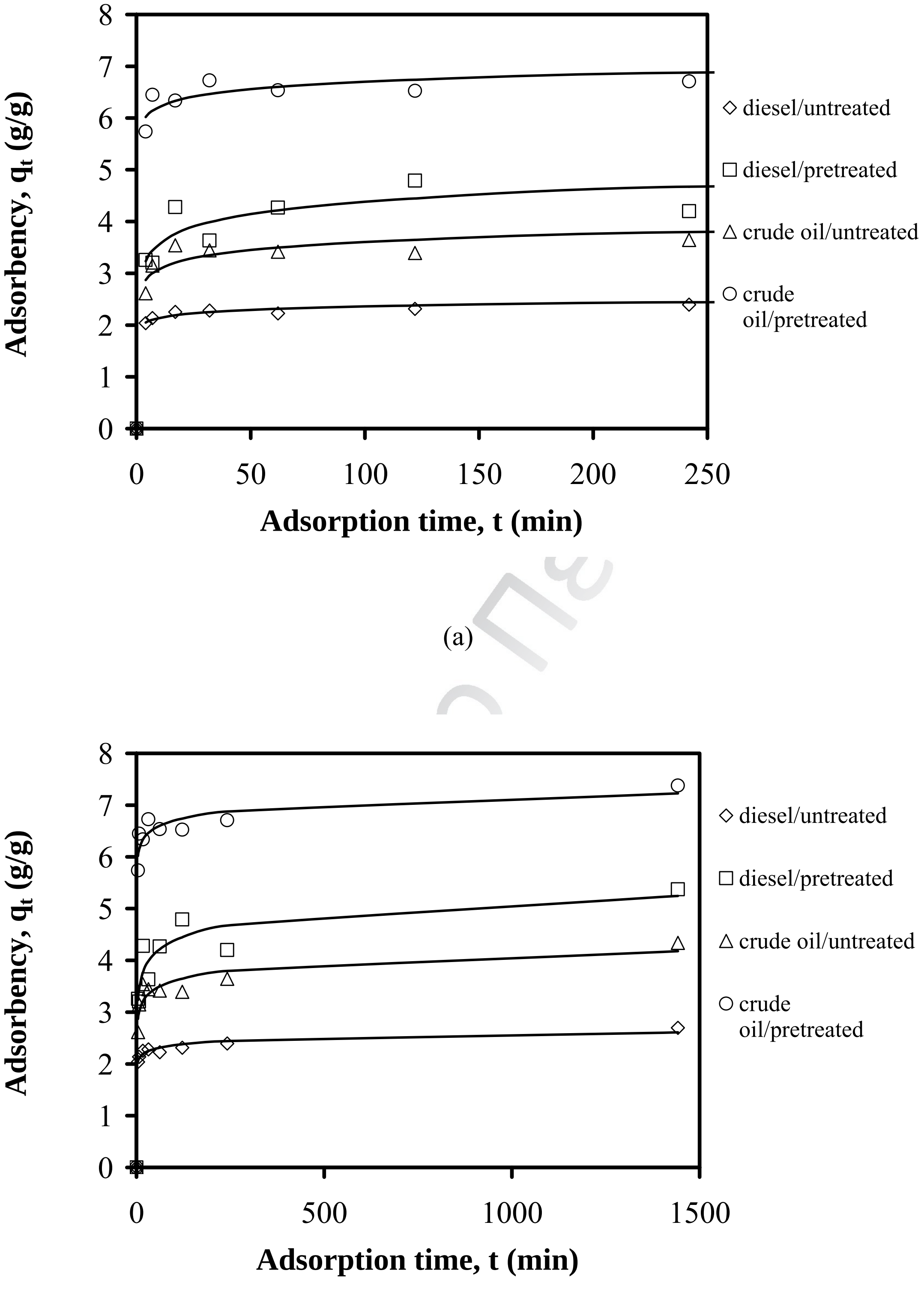


(a)



(b)

Fig. 11.12 Oil adsorbency for untreated and pretreated wheat straw vs. adsorption time: (a) for $t<250$ min and (b) for $t<1500$ min; two-parameter empirical kinetic model was applied



(a)

(b)

Fig. 11.13 Oil adsorbency for untreated and pretreated wheat straw vs. adsorption time: (a) for *t*<250 min and (b) for *t*<1500 min; three-parameter empirical kinetic model was applied

In Fig. 11.13, oil adsorption on wheat straw vs. adsorption time t: (a) for $t<250$ min and (b) for $t<1500$ min in the case of the three-parameter empirical kinetic model was shown, while in Table 11.15 sum, n', p', SEE and A, b, q values were performed.

Table 11.15 Three-parameter empirical kinetic model parameter values for oil adsorption on untreated and pretreated wheat straw

Case	Diesel/UWS	Diesel/AWS	Crude oil/UWS	Crude oil/AWS
sum	0.0277	0.8063	0.3309	0.3435
n'	8	8	8	8
p'	3	3	3	3
SEE	0.0745	0.4016	0.2572	0.2621
A	12.7012	12.2618	12.3926	10.6730
b	0.0078	0.0320	0.0195	0.0211
q	14.61	14.96	14.93	16.39

11.4 Discussion of kinetic results of oil (diesel oil and crude oil) adsorption

The NLRA estimate of the first order rate constant *k* was higher for AWS comparing to the UWS as regards crude oil adsorption presented in Table 11.5. The diesel and crude oil amount adsorbed after equilibrium time were significantly higher for the AWS (4.41 and 6.70 g/g, respectively) comparing to the UWS (2.35 and 3.63 g/g, respectively). As regards the model with fixed kernel q_0, the first order rate constant *k* was also higher for AWS comparing to the UWS in the case of crude oil adsorption presented in Table 11.6. The diesel and crude oil amount adsorbed after equilibrium time were the same, not affected by the presence of the fixed kernel q_0. In the case of first order kinetics, the model without fixed kernel q_0 gave lower SEE values.

The second order rate constant k_2 was higher for AWS comparing to the UWS as regards crude oil adsorption presented in Table 11.7. The diesel and crude oil amount adsorbed after equilibrium time were significantly higher for the AWS (4.62 and 6.82 g/g, respectively) comparing to the UWS (2.40 and 3.75 g/g, respectively). As regards the model with fixed kernel q_0, the second order rate constant k_2 was also higher for AWS comparing to the UWS in the case of crude oil adsorption presented in Table 11.8. The diesel and crude oil amount adsorbed after equilibrium time were the same, not affected by the presence of the fixed kernel q_0. In the case of second order kinetics, the SEE values where lower compared to those found for first order kinetics. Moreover, the second order model without fixed kernel q_0 gave lower SEE values.

The intra-particle rate constant k_p was significantly higher for AWS comparing to the UWS as regards diesel and crude oil adsorption presented in Table 11.9. As regards the model with fixed kernel q_0, the intra particle rate constant k_p was also higher for AWS comparing to the UWS for both diesel and crude oil adsorption presented in Table 11.10. The intra-particle diffusion model with or without fixed kernel q_0 gave SEE values significantly higher than the above mentioned kinetic models. In the case of intra-particle kinetics, the model with fixed kernel q_0 gave significantly lower SEE values.

The Elovich rate constant β was significantly higher for AWS comparing to the UWS as regards diesel oil adsorption presented in Table 11.11. The Elovich model gave SEE values significantly lower than the above presented kinetic models.

The fractional power function rate constant b was significantly higher for AWS comparing to the UWS as regards diesel oil adsorption presented in Table 11.12. The fractional power function kinetic model gave SEE values significantly lower than the Elovich kinetic model.

The one-parameter empirical constant b was higher for AWS comparing to the UWS as regards crude oil adsorption presented in Table 11.13. The diesel and crude oil amount adsorbed after equilibrium time were significantly higher for the AWS (5.37 and 7.38 g/g, respectively) comparing to the UWS (2.70 and 4.34 g/g, respectively). The one-parameter empirical kinetic model gave SEE values comparable to the other kinetic models.

The two-parameter empirical constant b was higher for AWS comparing to the UWS as regards diesel and crude oil adsorption presented in Table 11.14. The diesel and crude oil amount adsorbed after equilibrium time were the same independently of the presence of the second parameter. The two-parameter empirical kinetic model gave SEE values significantly lower than the one-parameter empirical kinetic model.

The three-parameter empirical constant b was higher for AWS comparing to the UWS as regards diesel and crude oil adsorption presented in Table 11.15. The diesel and crude oil amount adsorbed after equilibrium time were slightly higher for the AWS (14.96 and 16.39 g/g, respectively) comparing to the UWS (14.61 and 14.93 g/g, respectively). The three-parameter empirical kinetic model gave SEE values slightly higher than the two-parameter empirical kinetic model.

As regards the three above mentioned empirical kinetic models, all SEE-values were found lower than the first-order, the second-order and the intra-particle diffusion kinetic model's values, indicating the high applicability of these models to the adsorption of diesel oil and crude oil on UWS & AWS. On the other hand, lower SEE-values were found for the Elovich kinetic model while the lowest SEE-values were obtained for the fractional power function kinetic model indicating the highest applicability of the very last.

As a conclusion, from the kinetic models presented in chapter 11.2 the fractional power function kinetic model gave the lowest SEE values simulating the adsorption kinetics in all cases (i.e., diesel oil on UWS & AWS and crude oil on UWS and AWS). The adsorption rate is higher as regards the autohydrolyzed material comparing to the untreated material in the case of diesel oil. The diesel and crude oil amount adsorbed after equilibrium time was approximately two times higher for the AWS comparing to the UWS.

CHAPTER 12
CONCLUSIONS- ASPECTS FOR FURTHER RESEARCH

12.1 Conclusions

The proposed methodological framework (PNCP), as described in chapter 3, responds to marine pollution incidents on real time; provides clear and traceable solutions/alternatives methods into the decision-making process; considers ecological and socio-economical parameters; coordinates efficiently the Services involved; provides suitable procedures of oil spill identification caused by unknown source(s), and uses new technologies to the limit of their possibilities. The framework of the PNCP, can be used effectively to shorten considerably oil-spill incidences detection time thus allotting more precious time for decision making on appropriate combating. Furthermore, the degree and extent of each competent Service to be involved in incidence combat, along with the time/stage of involvement are clearly determined and appropriately documented (Table 2.3), resulting in a more rapid and effective coordination of the participating authorities.

It can be therefore concluded that the implementation of the proposed framework for dealing with the “Sitarem-Spirit” incidence, (analysed in chapter 4), would have significantly reduced the impact of the pollution. The oil spill, would have been located immediately either by SAR imagery or “Poseidon” floating sensors indications, (presented in chapter 3), permitting an immediate response to the incident. Following the cascade of activities shown in Fig. 3.1, an immediate selection of anti-pollution method alternatives (oil containment-recovery, use of oil booms, chemical dispersants etc.) could be achieved, possibly resulting to a complete-immediate pollution combating. Based on “Poseidon” data, complete and precise data of weather conditions, oceanographic parameters and hydrodynamic traffic of this specific sea area would be available and suggestive of favourable conditions for the use of chemical dispersants (shipboard and portable), effectuated either immediately or at the 5-days-later window, inhibiting the large scale oil spill dispersion. Using the “GNOME” model, (presented in chapter 3), calculated for the real data (accurate location, type/ size of oil spill, wind speed and direction, etc.), a clear image/ evaluation of pollution movement for a period of 7 days would be available, indicating for the above mentioned case study, Diakofti Kythira coastline as the target. The protection measures that could have been taken are: oil booms deployment and use of absorbents in order to avoid the coastline pollution; oil containment – recovery by using oil skimmers and pumps; placement of efficient number personnel (HCG's, local Authority Organization's, volunteers) and anti-pollution means/ equipment; immediate oil products cleaning of coasts that might be washed out ashore, and provision of storage spaces for the collected above mentioned oil products. Generally, as a computer-aided decision-making tool, the proposed methodological framework helps to handle efficiently the entire oil spill emergency management life cycle.

As it was mentioned in chapter 6, where a MCA regarding oil adsorbents selection was introduced, the scope of this study was not to provide a detailed feasibility analysis regarding oil adsorbents selection; but to answer the question of how to select an oil adsorbent obtained from modified lignocellulosic or commercial adsorbents. In this sense, the study aimed at demonstrating efficient and effective way for selecting the most efficient oil adsorbent. This rationale comes within the recently developed area of integrated oil spill management that reflects the multi purpose management of oil adsorbent selection aligned more or less to the oil spill recovery.

The auto-hydrolysis pretreatment increased the hydrophobicity of straw. The removal of the hemicelluloses and the amorphous cellulose increased the lignin content of the material. Moreover, it opened the lignocellulosic micro structure. Auto-hydrolysis at very severe conditions destroyed the macro structure of the straw particles, making it less floatable and unsuitable for oil spill cleaning by decreasing its sorption capacity. The modification process of auto-hydrolysis is cost-effective, because uses only tap recyclable water without the presence of any chemicals (acids, salts, bases, organic solvents). The modification expenses can be covered by the co-produced fermentable sugars for the bio-ethanol production industry (Sidiras et al., 2011a). Furthermore, the thermal energy needed for the auto-hydrolysis process can be supplied by solar systems which are subsidized through E.U. funds as renewable energy sources. Although Greece, as a South-Eastern Mediterranean Country, has long sunshine periods all year round, solar radiation for this purpose is adequate even in the Central-Northern European Countries. Moreover, since wheat straw is an agricultural residue that can be used for waste-water treatment by adsorption, while no chemicals are required to be added, auto-hydrolysis modification of the adsorbent may be considered to take place in the Industrial Ecology framework.

The adsorbency-values were simulated by a proposed herein novel model incorporating the auto-hydrolysis severity factor R_0. In this work, treatments were carried up to reach maximum temperatures in the range 160–240^{o}C. Diesel and crude oil were used as oil pollutants and the experiments were carried out in pure liquids and in oil spills on fresh and seawater. Diesel and crude oil adsorbencies were simulated according to the proposed novel model and found to reach a maximum by optimizing the auto-hydrolysis conditions. These conditions could be 200^{o}C for time 10 min isothermal reaction time (i.e., log R_0=5.15) giving: (i) diesel adsorbency up to 6.1 g/g, crude oil adsorbency up to 8.4 g/g, RDA=84% and RCA=75% in the case of oil spill on freshwater and (ii) diesel adsorbency up to 6.7 g/g, crude oil adsorbency up to 6.9 g/g, RDA=71% and RCA=80% in the case of oil spill on seawater. The autohydrolyzed wheat straw can be used as low cost adsorbent for oil spill cleaning. In sub-chapter 6.3.1 the autohydrolyzed wheat straw was estimated that could be sold at the price of 0.164 €/kg. It was suggested the co-production of ethanol and adsorbate according to the bio-refinery frame. In sub-chapter 6.3.5, it was mentioned that the price for polypropylene oil absorbent pads is 6.01 €/kg. Subsequently, it is more than obvious the superiority of the autohydrolyzed wheat straw as adsorbent in economic terms.

12.2 Aspects for further research

In this sub-chapter aspects for further research are presented in order to improve the proposals of the Thesis.

- More case studies with the implementation of the two plans in real incidents should be analysed for the evaluation of the plans (PNCP and GNCP) and their comparison.
- By the use of satellite remote sensing a continue surveillance of the real incident described in chapter 4, and pollution spreading-movement would have been achieved despite of the existing weather conditions. Funds should be invested on SAR satellite imagery technology for oil spill detection and surveillance. Moreover, PNCP could be the basis for further research as satellite technology has only recently started in Greece.
- The network of the observation buoys could be linked to the Regional Pollution Combating Centers net (Fig. 2.1). “Poseidon” and “GNOME” model

could be used as peripheral tools, connected to the Proposed National Contingency Plan, and continuously give information concern meteorological - sea conditions prevailing in the area of imaginary oil spill incident and a clear image/ evaluation of the pollution movement.

- The knowledge base in Microsoft Access form could be enriched for further research. This knowledge base includes data about adsorbents that were used, the kind of pretreatment, the oil type, the adsorbency, the media in which this adsorbency was measured , the authors names, the title of the study, the name of the referred journal and the year of publication. Adsorption isotherms on autohydrolyzed wheat straw should also be conducted.
- Other biomass materials like corn stover, rice straw, pine sawdust etc. could be investigated by experimental measurements relevant to their possible usage as oil adsorbents with comparatively high sorption capacity, biodegradability and cost-effectiveness for cleaning an oil spill in seawater.
- Other pretreatment methods like maleic acid treatment, NaOH treatment etc. could be examined by experimental measurements relevant to their possible improvement of the initial adsorption capacities of the above mentioned materials. These modified materials should be compared to commercial and already studied materials.
- The effect of the increase/ decrease of the adsorbent weight, of the chemical dispersant dose in oil spill experiments and the effect of different adsorbent time on autohydrolyzed wheat straw's adsorptivity should also be studied.

In general, funds should be invested to improve the efficiency of the Proposed National Contingency Plan in order to interconnect it with necessary peripheral tools. Furthermore, new series of experiments should be designed and executed for the research on efficient novel biomass materials as oil adsorbents and for their modification processes in order to improve their adsorption efficiency. Finally, as theoretically demonstrated in chapter 6, autohydrolyzed wheat straw, could be efficient and effective adsorbent for oil products recovery. However, it should be stressed that the rationale for proposing this oil adsorbent need to be further underpinned by the implementation of market analysis and feasibility study in order to clearly prove the economic reasonability and viability of this adsorbent.

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